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Morphological Transformations of Native Petroleum Emulsions.

I. Viscosity Studies

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Abstract

Emulsions of water in as-recovered native crude oils of diverse geographical origin evidently possess some common morphological features. At low volume fractions ϕ of water, viscosity behavior of emulsions is governed by the presence of flocculated clusters of water droplets, while characteristic tight gels, composed of visually monodisperse small droplets, are responsible for viscosity anomaly at $\phi \approx 0.4-0.5$. Once formed, “small-droplet” gel domains apparently retain their structural integrity at higher ϕ , incorporating/stabilizing new portions of water as larger-size droplets. The maximum hold-up of disperse water evidently is the “close packing” limit of $\phi \approx 0.74$. At higher water contents (up to $\phi \approx 0.83$) no inversion to O/W morphology takes place, but additional water emerges as a separate phase. The onset of stratified flow (W/O emulsion gel + free water) is the cause of the observed viscosity decrease, contrary to conventional interpretation of viscosity maximum as the reliable indicator of emulsion inversion point.

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1. Introduction

The production of crude oil emulsions during petroleum recovery is a ubiquitous and increasingly problematic phenomenon in the oil industry. The resolution of such systems can be a technical and financial burden to the industry as a whole, resulting in reduced production time, operating/processing problems and heavy costs incurred through the application of a combination of mechanical/chemical/electrical treatment programs. Petroleum emulsions readily form from water/oil mixtures in turbulent flows or due to pressure gradients in reservoir pores, in the chokes at the wellheads and in various valves in piping used for oil production.

A good knowledge of native petroleum emulsions is necessary for controlling/prevention of emulsification processes and for improving de-emulsification technologies, hence many experimental/theoretical studies have been carried out in the last decades.^{1,2} However a lot of publications report data obtained only with “synthetic emulsions”, specially formulated to support some theoretical model,^{3,4} while studies with emulsions of native crudes are frequently aimed merely at improving some new experimental techniques.⁵ As a result of preferential attention to multiple “fine details”, the existence of some common features of native crude oil emulsions still remain unnoticed, under-investigated, or unexplained. E.g., it is rarely emphasized that virtually all (more than 95%) of the native crude oil emulsions formed in the oil field as well as infamous “chocolate mousses” in oil spills are of the same water-in oil (W/O) type.⁶⁻⁸ Qualitative explanation of the preference of W/O morphology is that native crude oils contain certain “indigenous surfactants” such as asphaltenes, resins, naphthenic acids and oil-wet fine solids,⁹ while, according to Bancroft’s rule, the liquid in which the surfactant is soluble becomes the continuous phase. These surfactants presumably migrate to the oil-water interface and stabilize water droplets by steric and electrostatic interactions, or by rigid-film forming.¹

Recently, it has been realized, that interfacial material in petroleum emulsions should be regarded as a certain additional “phase” (“third phase” in terminology of Ese et.al.¹⁰ or “D-phase”, as defined by Havre and Sjöblom¹¹). Some compositional and structural properties of interfacial phase have been determined by studies of specially formulated emulsions¹¹, and by monitoring “rigid film” properties at individual water droplets.^{12,13} In studies of “synthetic” diluted bitumen emulsion it was observed that “interfacial phases” containing fine solids and asphaltenes may attain more complicated morphology by incorporating small water droplets.¹⁴ However, in spite of continuing research, structure and function of interfacial phases in emulsions of native, as-recovered crude oils still remain under-investigated. Our previous studies¹⁵ have indicated that in native emulsions “interfacial phases” may exhibit a common, “small-droplet”, morphology and may act as stabilizing media for larger water droplets. The present paper gives new information with respect to the characteristics of water-in-native crude oil emulsions and, hopefully, can be used to obtain insight in underlying mechanisms of their flow behavior and stabilization mechanisms.

2. Materials and Methods

2.1. Materials. The virgin crude oil, in the following referred to as Oil 1 (O1), was collected directly from the producing well #624 at Korobkovskoye reservoir (Volgograd, Russia), had a density of 832 kg/m³, a pour point below -18 °C, contained ca. 1 wt.% asphaltenes, 8 wt.% resins, 2 wt.% waxes, suspended fine solids not exceeding 0.4 g/L. Oil samples were stored in the dark, in air. The water in this study was a double distillate stored in air, with pH≈5.5. In emulsion studies, samples of 10 g water + O1 oil were prepared at various weight ratios ranging from 0 to 85% (weighting accuracy 0.01 g) in standard cylindrical glass

vessels. The two phases were mixed manually by vigorously shaking and upturning a vessel (with a frequency of $\sim 2\text{-}2.6\text{ c}^{-1}$) for 10 minutes, which resulted in a visually homogeneous emulsion. It should be noted, that some emulsion specialists may regard such method of emulsification as too “gentle”, as compared with the use of high-speed blade mixers or ultrasound techniques in laboratory experiments.² However, “gentle” conditions of emulsification are more frequently encountered in petroleum recovery operations as well as in oil spill evolution.⁶⁻⁹ Moreover, the employed manual method has ensured a reproducibility in the droplet size distribution, as will be further substantiated in Part II of this publication.

A type of emulsion (W/O or O/W) was inferred by a conventional “drop test”.¹⁶ (a drop of o/w emulsion disperses in water, while a drop of w/o emulsion disperses in oil). All our emulsions, with water contents up to 85% w/w, appeared to be oil-continuous (W/O).

2.2. Shear Viscosimetry. Flow curves of emulsions (shear stresses as functions of shear rates) were determined using: (1) a Brookfield DV-II+ PRO Digital Viscometer, equipped with a concentric cylinder ULA setup (spindle diameter=25.15 mm, gap= 1.23 mm), at shear rates from 0.06 to 100 s^{-1} ; (2) a Rheotest 2.1 VEB MLW Viscometer, with a concentric cylinder S-S1 setup (spindle diameter=39.2 mm, gap= 0.4 mm), at shear rates from 0.05 to 437 s^{-1} . As a standard precaution to minimize possible wall slip,² cylinder surfaces were pre-treated with rough sandpaper. Temperature was controlled at 20 °C by a circulating water bath, typically to within 0.2 °C. When first loaded into the viscometer, each sample was pre-sheared by applying a lowest shear rate for 3 min. The emulsion flow curves were measured as the shear rate was increased in steps. At each shear rate, the samples were equilibrated for 1 min prior to the measurement. Using this protocol, we obtained reproducible flow curves.

3. Experimental Results and Discussion

3.1. “Raw” Experimental Data. The measured dependencies of shear stresses on shear rates (flow curves) for emulsions of Oil 1 with water volume fractions ϕ ranging from 0 to 0.825 are shown in Figures 1,2. Plotting flow curves on logarithmic axes facilitates comparison of samples with parameters varying over several orders of magnitude.

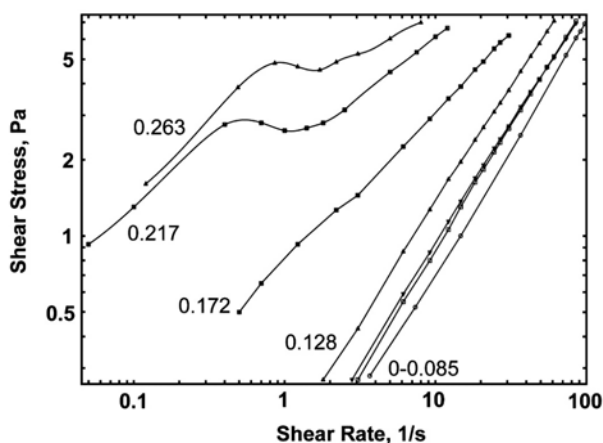


Figure 1. Flow curves for emulsions in Oil 1 with low volume fractions of water (indicated in the Figure). Large-gap Brookfield Viscometer.

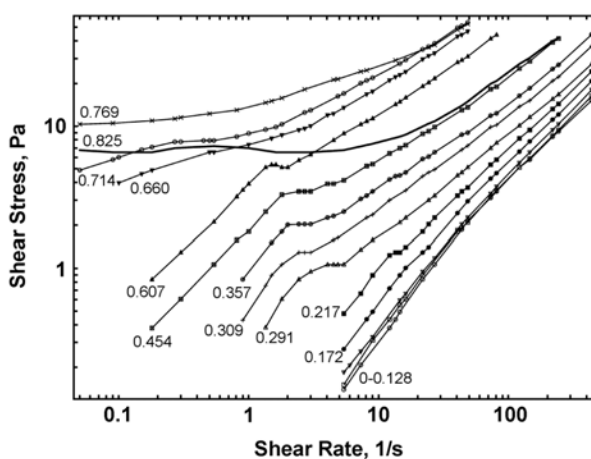


Figure 2. Flow curves for emulsions in Oil 1 with a wide range of water volume fractions (indicated in the Figure). Small-gap Rheotest Viscometer

On a log-log plot, straight-line segments of the curves indicate validity ranges of a frequently employed Power Law (Ostwald–de Waele) flow model:¹⁷

$$\tau = K\dot{\gamma}^n \quad (1)$$

where n is the “flow behavior index” and K is the “flow consistency index”. Note, that for $n = 1$, the model reduces to that of a Newtonian fluid, with viscosity $\eta = K$. Figures 1,2 show that for all emulsions with $\phi \leq 0.607$ low-shear segments of flow curves are fairly parallel (and correspond to Newtonian flow - cf. Section 3.2). Apparent distortion of low-shear flow curves at $\phi = 0.660$ and at higher water contents is due to an appearance of a noticeable yield stress (cf. Figure 3.).

Flow behavior of emulsions at higher shear rates changes qualitatively around a characteristic water volume fraction ϕ^* , which depends on the viscometer’s gap size (for a gap of 1.23 mm in Figure 1, $\phi^* \approx 0.14$, while for a gap of 0.4 mm in Figure 2, $\phi^* \approx 0.21$). For $\phi < \phi^*$ flow curves exhibit a gradual increase of shear stress with the increase of shear rate. At water contents above ϕ^* , however, a stress “plateau” develops, clearly delimiting low-shear and high-shear regimes. For a given ϕ , an onset of the plateau (departure from Newtonian behavior) evidently shifts to lower shear rates as the viscometer’s gap is increased. An increase in disperse phase volume fraction leads to systematically higher values of the “critical” stress at the plateau. Characteristic stress plateaus following Newtonian regimes are attributes of viscoplastic materials and are frequently observed in studies of flocculated/attractive/adhesive emulsions.^{18,19} Stress plateau in emulsions are usually attributed to breakdown of space-filling gel networks, while the width/slope of the plateau reflects the uniformity of the gel structure.²⁰ Accordingly, the data of Figure 2 suggest that the most uniform emulsion gels form at water fractions $0.36 \leq \phi \leq 0.61$. Abrupt increase of the plateau width (distortion of gel uniformity) is observed for $\phi = 0.66$ which is fairly close to the maximally random jammed (MRJ) volume fraction of

droplets,²¹ $\phi_{MRJ} = 0.64$ (previously referred to as random close packing). As expected, at $\phi \geq \phi_{MRJ}$ emulsion gels become “compressed”²² and both release of strain and break-up of bonding in the gel structure commence at the lowest shear rates studied.

For water contents above $\phi=0.74$ (hexagonal close packing of monodisperse spheres), flow curves of emulsions exhibit a new peculiar feature, namely they intersect lower- ϕ curves at high shear rates. To highlight this behavior, the data for $\phi=0.825$ are shown by a thick solid line in Figure 2. Visual inspection revealed that such peculiar behavior was due to “squeezing” of free water from emulsion gels. It should be emphasized that even the “partially dehydrated” gels always remained of the W/O type and an inversion to O/W emulsions never has been observed.

Flow curves at high shear rates for all other emulsions with $\phi \leq 0.714$ exhibit qualitative similarity - fairly parallel straight-line segments on log-log plots (power law flow). There is a slight fanning of these segments due to variations of the flow behavior index from $n \approx 0.95$ for $\phi \leq 0.1$ to $n \approx 0.65$ for $\phi = 0.6-0.7$. In fact, flow evolution of all broken gels with $0.2 \leq \phi \leq 0.7$, appears to be similar not only qualitatively but also quantitatively when analyzed in terms of “excess” shear parameters, originating from respective gel-break points (cf. Section 3.3).

In the following sections we discuss in more detail the flow behavior of emulsions in low-shear, plateau and high-shear ranges.

3.2. Analysis of Low-Shear Regime. As indicated above, all low-shear segments of flow curves may be characterized by a common flow behavior index $n=1$. To verify the validity of a “true” viscosity η , defined by the Newtonian model:

$$\tau = \eta \dot{\gamma} , \quad (2)$$

we have also approximated the discussed segments with the Bingham’s equation:¹⁷

$$\tau = \tau_0 + \eta_P \dot{\gamma} , \quad (3)$$

where τ_0 is an “apparent yield stress” and η_P is a Bingham’s “plastic viscosity”.

As illustrated by curve (b.) in Figure 3, τ_0 acquires non-zero values only in emulsions with $\phi \geq 0.660$, hence at all lower volume fraction of water Newtonian and Bingham’s viscosities are virtually identical. The analysis of volume fraction effects in emulsions usually is performed in terms of the “relative viscosity” $\eta_{REL} = \eta/\eta_0$, where η and η_0 are viscosities of the emulsion and of the parent crude oil, respectively.¹⁸⁻²⁰ Accordingly, data set (a.) in Figure 3 shows the effects of volume fraction of water on low-shear relative viscosities evaluated from flow curve measurements in the small-gap Rheotest Viscometer (note the log scale for η_{REL}).

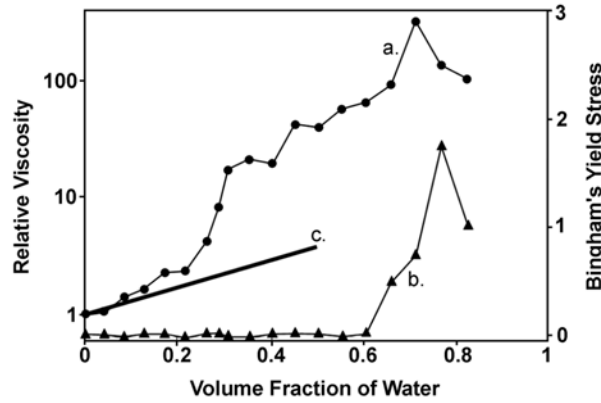


Figure 3. Effects of volume fraction of water in Oil 1 on: **a.** – low-shear relative viscosity of W/O emulsions; **b.** – low-shear apparent yield stress. The original flow curves were obtained in the small-gap Rheotest Viscometer (cf. Figure 2). Solid line **c.** represents the Batchelor’s approximation, expressed by Eq.(5).

There are several phenomenological theories purporting the dependence of the viscosity of suspensions/emulsions on volume fraction of the disperse phase ϕ .¹⁷ Many of these originate from the Einstein relation for spherical particles in the dilute limit:

$$\eta_{REL}(\phi) = 1 + 2.5\phi \quad (4)$$

Contributions due to hydrodynamic interactions and Brownian motion may be accounted for by a second-order term, as shown by Batchelor:^{23,24}

$$\eta_{REL}(\phi) = 1 + 2.5\phi + 6.2\phi^2 \quad (5)$$

Here the factor of 6.2 is appropriate for the low-shear limit with the predominance of Brownian motion,²³ while in the high-shear limit where the hydrodynamic contribution dominates, this factor reduces to 5.2.²⁴

As a result of consideration of finite particle sizes, a new “crowding” parameter was introduced into $\eta(\phi)$ models, namely that of “maximum packing fraction” ϕ_{max} . For fairly monodisperse emulsions/suspensions, it is a common practice to identify ϕ_{max} with “glass transition volume fraction”¹⁹ $\phi_G \approx 0.58$, “maximally random jammed volume fraction”²¹ $\phi_{MRJ} \approx 0.64$, or with “h.c.p. close packing” of spheres²⁵ $\phi_{HCP} \approx 0.74$. The most famous in this class of models is the empirical (but later verified theoretically) Krieger- Dougherty relation:²⁶

$$\eta_{REL}(\phi) = \left(1 - \frac{\phi}{\phi_{max}}\right)^{-2.5\phi_{max}} \quad (6)$$

Mooney²⁷ also considered crowding effect of the dispersed phase and formulated the semi-empirical equation, which for spherical particles reduces to:

$$\eta_{REL}(\phi) = \exp\left(\frac{2.5\phi}{1 - \phi/\phi_{max}}\right) \quad (7)$$

Comparison of experimental data in Figure 3 with the above models shows that low-shear η_{REL} in the studied emulsions increases much more rapidly with ϕ than predicted by any of the equations (5-7). As an example, line (c.) in Figure 3 illustrates $\eta_{REL}(\phi)$ dependence according to Batchelor’s model (Eq. 5). Systematic diversion of experimental and theoretical $\eta_{REL}(\phi)$ data in the dilute regime most often is ascribed to clustering/flocculation of emulsion droplets and is interpreted in terms of (shear dependent) “effective volume fraction” of clusters/flocs $\phi_{eff} > \phi$.^{28,29} Higher volume fractions of flocculated disperse phase (in our case – water) are due to

“immobilization” of the continuous phase (in our case – oil) inside clusters.²⁹ The relative amount of immobilized oil is the lowest in clusters of densely packed water droplets and increases in loosely packed (e.g., fractal) clusters. The “internal volume fraction” of water droplets in clusters $\phi_{\text{int}} = \phi/\phi_{\text{eff}}$ may be employed as a quantitative measure of the density of packing.³⁰ Figure 4 shows that there is a variety of possible ϕ_{int} already in clusters with small numbers of flocculated water droplets.

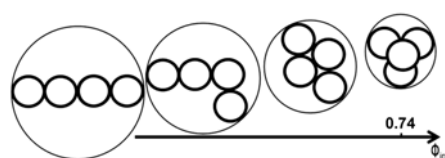


Figure 4. A variety of packing configurations in clusters of four flocculated droplets.

The degree of clustering in the studied emulsions was evaluated by substituting $\phi_{\text{eff}} = \phi/\phi_{\text{int}}$ instead of ϕ into equations (5-7) and fitting the modified equations to experimental low-shear $\eta_{\text{REL}}(\phi)$ data sets with ϕ_{int} as an adjustable parameter. The fitting procedure was performed for emulsions with $\phi < 0.13$, in an assumption of negligible cluster fragmentation at small shear rates. The results of this analysis are presented in Table 1.

Sufficiently high coefficients of determination confirm the constancy of ϕ_{int} at low volume fractions of water and the reliability of systematically higher ϕ_{int} observed in the small-gap viscometer, irrespective of the employed fitting model. The respective values of ϕ_{int} suggest a presence only of densely-packed clusters of water droplets in “severe” low-gap conditions, while in the less constrained large-gap flow loosely-packed big clusters are also retained.

Table 1. Internal volume fraction of water droplets in flocculated clusters for two different-gap viscometers (emulsions with volume fraction of water below 0.13).

Model	ϕ_{\max}	Gap, mm	ϕ_{int}	R^2
Batchelor	-	1.23	0.550	0.923
		0.40	0.645	0.907
Krieger-Dougherty	0.74	1.23	0.592	0.942
		0.40	0.719	0.920
	0.64	1.23	0.602	0.944
		0.40	0.741	0.922
	0.58	1.23	0.613	0.945
		0.40	0.752	0.924
Mooney	0.74	1.23	0.654	0.948
		0.40	0.794	0.942
	0.64	1.23	0.680	0.950
		0.40	0.826	0.946
	0.58	1.23	0.699	0.952
		0.40	0.847	0.949

At higher ϕ cluster sizes no longer remain constant as evidenced by large departures from any of the above models (Eq. 5-7). To highlight this departure from smooth theoretical dependencies we found it useful to re-scale the measured emulsion viscosities via dividing the experimental $\eta_{\text{REL}}(\phi)$ data set (Figure 3) by Mooney's approximation with $\phi_{\max}=1$, namely by $\eta_{\text{REL}}=\exp[2.5\phi/(1-\phi)]$. The respective re-scaled viscosities for low-shear conditions are shown by filled symbols in Figure 5. The horizontal straight line is the "ideal" Mooney behavior as predicted by Eq.(7). As described above, systematic departure of experimental viscosities from this behavior at $\phi<0.13-0.15$ may be attributed to flocculation of water droplets into fairly stable/independent clusters, as indicated by a constancy of ϕ_{int} . Structural features of the disperse phase in this regime of freely moving "dilute clusters" are schematically illustrated in Figure 6A (after Ref. 31). A local maximum of re-scaled viscosity at $\phi\approx 0.12$ may be attributed to a transient "dynamic percolation" of clusters.³² In emulsions of non-flocculated droplets percolation phenomena are usually observed at volume fractions of the dispersed phase close to 0.16-0.20.^{33,34} In dispersions of clusters, these values should be characteristic for "effective volume

fractions” – e.g., in case of spherical densely-packed clusters ($\phi_{\text{int}}=0.74$) the respective phenomena may be expected at $\phi \approx 0.12-0.15$.

The second, intense, maximum in Figure 5 (at ϕ around ca. 0.4) may be identified with “glass transition volume fraction”.¹⁹ In non-flocculated dispersions $\phi_G \approx 0.58$, the same value should be ascribed to “effective volume fraction” in dispersion of clusters. In the above case of spherical densely-packed clusters ($\phi_{\text{int}}=0.74$), the “glass transition” phenomena may be expected at $\phi \approx 0.43$.

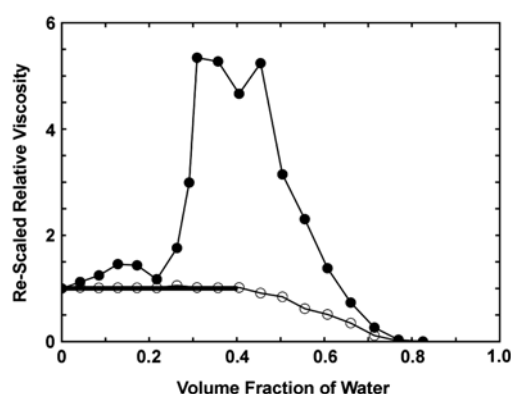


Figure 5. Experimental viscosities of W/O emulsions re-scaled via dividing by Mooney approximation. Filled symbols – low shear regime; open symbols – high shear regime ($\tau=45$ Pa). The horizontal straight line shows the “ideal” Mooney behavior.

At the “glass transition”, diffusing clusters become “crowded”,^{31,35} i.e. they are trapped in transient cages formed by their nearest neighbors and diffusion is no longer possible - cf. Figure 6B. The result of such confinement is that clusters no longer can be regarded as individual entities. Not only intra-cluster, but also inter-cluster bonds are formed between flocculating water droplets and the emerging disperse phase morphology is that of a 3D emulsion-gel network, spanning throughout the sample^{18,31} – cf. Figure 6C. The bonds between water droplets both in the “dilute clusters” and in the gel morphologies apparently are weak enough to be easily

broken by increasing shear rates/stresses. As an illustration, open symbols in Figure 5 show re-scaled viscosities of emulsions for a shear stress of 45 Pa (cf. Figure 11). Note the absence of “dilute cluster” and “emulsion-gel” anomalies and the validity of Mooney approximation expected for a suspension of individual non-flocculated droplets. In more detail, break-up of droplet clusters will be discussed below, in Section 3.3.

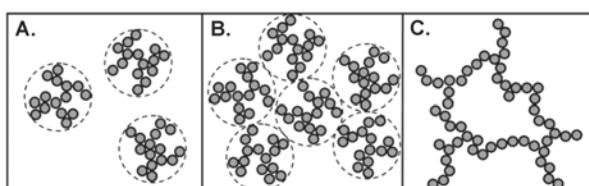


Figure 6. Apparent evolution of low-shear emulsion morphology with increasing water content. A. – “Dilute clusters” of flocculated water droplets. B. – “Crowded clusters”. C. – Space-filling “emulsion gel”. (After Ref. 31).

For direct visualization of the above discussed cluster/gel morphologies we employed optical microscopy of freshly prepared W/O emulsions in Oil 1. The details of these experiments and the results of droplet size, sedimentation, density and optical analysis will be reported in Part II of this publication. Representative images in Figure 7 clearly show the presence of compact “dilute” clusters of water droplets at small ϕ (A), transient percolation into loose branched structures (B), and spanning networks of gel-emulsion at higher volume fractions (C,D).

Note that “initially-formed” gel emulsions at ϕ just below and close to 0.4 are composed of visually monodisperse small droplets with a number average diameter of ca. 10 μm . Such fairly uniform structures evidently are responsible for strong peaking of re-scaled viscosity in Figure 5. In emulsions with higher ϕ (Figure 7D) additional water is entrapped into this “small-droplet gel” in the form of larger-size drops, which distorts uniformity of the structure and reduces re-scaled viscosity at high water contents.

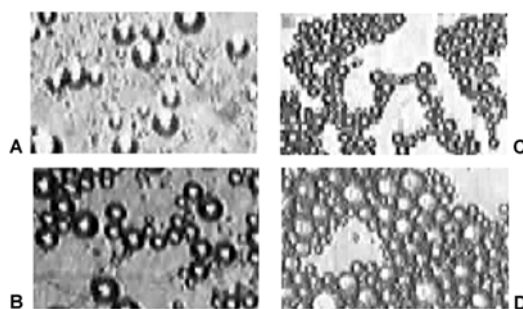


Figure 7. Microscopic images of freshly-prepared W/O emulsions in Oil 1 with different water contents: A - $\phi=0.085$; B - $\phi=0.263$; C - $\phi=0.357$; D - $\phi=0.607$. The width of all rectangular areas is $\sim 220 \mu\text{m}$.

Our microscopy/sedimentation studies indicate that the above discussed “small-droplet” gel structures play a crucial role in determining morphological and other properties of native petroleum emulsion. These structures exhibit considerable mechanical strength and could not be broken by centrifuging at 1000g for 20 minutes. The “oil-in-gel” phase is remarkably different from the “free oil” phase in the remaining parts of emulsion. “Oil-in-gel” apparently is enriched in high-MW constituents (as revealed by spectrometry and refractometry) and possesses density at least 7-8% higher than that of “free oil” phase and of the parent crude oil. The density mismatch can not be attributed solely to partitioning of high-MW fractions. Emergence of some new molecular structuring in “oil-in-gel” is indicated by a noticeable “excess density” of entire emulsion as compared to the value predicted by ideal mixing rule.

To conclude this section, it should be emphasized that the double-peak viscosity anomaly of the type shown in Figure 5 appears to be a universal feature of native W/O petroleum emulsions, as revealed by similar re-scaling of emulsion viscosities from available publications.^{15,36-39} Table 2 shows the diversity of oil origins, W-O phase properties and experimental conditions in these experiments. However, after re-scaling (like that in Figure 5),

all data sets reveal qualitatively similar viscosity anomalies, peaking at water volume fractions somewhat below 0.2 and close to 0.4, as illustrated in Figure 8. (Note that for clarity of presentation some curves are shifted upwards along the vertical axis, namely, curves b and h – by 0.5, curve c – by 1.0). We ascribe this viscosity similarity to common cluster/gel morphologies apparently inherent to native petroleum emulsions.

Table 2. Properties of crude oil and water (brine) phases employed for studies of W/O emulsions in various publications. The last two columns indicate conditions of reported viscosity measurements.

Crude oil origin	Oil density*, kg/m ³	Oil viscosity*, mPa·s	Asphaltenes in oil, wt %	Resins in oil, wt %	Waxes in oil, wt %	Brine/water density*, kg/m ³	T, °C	Shear rate, 1/s
a. Russia ¹⁵	902.2	70	8.89	19.25	5.59	1154	30	<20
b. Russia ¹⁵	905.1	76	3.03	12.65	1.96	1148	30	<20
c. Russia ¹⁵	906.0	43	5.35	9.75	12.42	1148	30	<20
d. Brazilia ³⁶	868.7	10	1.09	n/a	n/a	1027	20	100
e. Brazilia ³⁶	898.1	51	2.33	n/a	n/a	1001	20	100
f. Brazilia ³⁷	n/a	28	n/a	n/a	n/a	n/a	50	50
g. Malaysia ³⁸	793.4	6.2	0.4	5.2	2.4	1001	30	n/a
h. Russia ³⁹	858.8	804	n/a	n/a	n/a	n/a	20	3

* at 20 oC

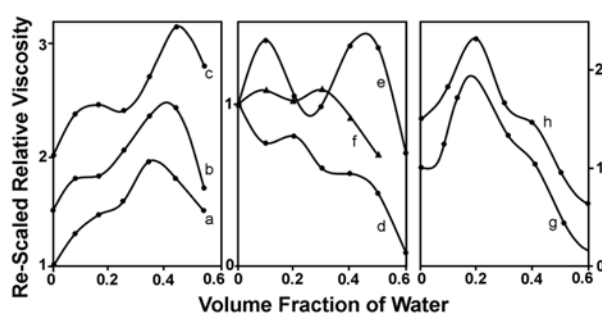


Figure 8. Apparent universality of cluster/gel morphology transformations of W/O emulsions in native crude oils from diverse geographical/geological locations (data specification - in Table 2).

For further support of common occurrence of tight “nearly monodisperse emulsion gel” structures we may refer to our earlier observations of “excess density” at $\phi \approx 0.4$ in twelve

different emulsions of saline reservoir brines in as-recovered native crude oils.¹⁵ These tight emulsion-gels has been also observed by direct microscopic observation of emulsions of tap water in a crude oil with properties substantially different from those of the above Oil 1 (namely: $\rho=915 \text{ kg/m}^3$; 3.3 wt.% asphaltenes; 24.8 wt.% resins; 2.5 wt.% waxes, suspended solids $\approx 0.6 \text{ mg/L}$).¹⁵

3.3. Analysis of Plateau and Higher Shear Regimes. In discussion of Figures 1 and 2, “stress plateau” in the measured flow curves we attributed to breakdown of emulsion-gel structures. The corresponding “gel break” stress τ_{GB} was evaluated as the highest value of τ at the onset of departure from low-shear Newtonian behavior. Figure 9 shows evolution of τ_{GB} in emulsions with increasing water contents for two viscometers with different gap dimensions.

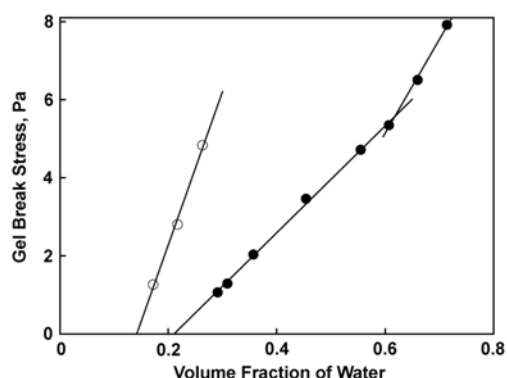


Figure 9. Gel-break stresses for W/O emulsions in Oil 1. Open symbols - large-gap (1.23 mm) Brookfield viscometer. Filled symbols - small-gap (0.4 mm) Rheotest viscometer.

Extrapolations of data sets in Figure 9 to zero τ_{GB} provide characteristic volume fractions ϕ^* at which gap-spanning gels start to form (cf. also discussion of Figures 1 and 2). Namely, for the large-gap viscometer $\phi^*=0.142$, while for the small-gap one $\phi^*=0.210$. The following linear dependence $\tau_{GB}(\phi)$ is indicative of uniformity of increasing volume of gel domains in decreasing

volume of “free oil” (cf. previous Section) and of apparently negligible contribution of water droplets not incorporated into gel structures. The departure from linear behavior is observed only in absence of “free oil”, for ϕ exceeding the “maximally random jammed” volume fraction of water droplets $\phi_{MRJ} \approx 0.64$.

One of the reviewers of this paper indicated that gap size effects in Figure 9 may be interpreted on the basis of “wall slipping” frequently observed in concentrated emulsions. Indeed, such interpretation may be feasible. However it should be emphasised that while for particle dispersions boundary surface “wall slip” is an experimental artefact eliminated in properly constructed rheometers,⁴⁰ for destructing gels some “volume slip” effects may be inherent (though gap-dependent) properties of the studied systems. In particular, gel fracture commences with “crack” propagation and disentanglement of fairly large gel “islands”,^{18,41} which in shear flow may slip with respect to each other and rotate along the shear applied, thus decreasing the measured viscosities. Moreover, characteristic plateau at flow curves have been shown to appear at flow curves due to “log-rolling” movement of emulsion flocs.⁴²

A common procedure in studies of viscoelastic (e.g., gel-forming) systems is to analyze structural break-up not in terms of flow curves but in terms of viscosity - shear stress behavior.¹⁹⁻

²¹ Accordingly, in Figure 10 we present $\eta_{REL}(\tau)$ dependencies for emulsions with $0.291 < \phi < 0.607$, which exhibit distinct gel-break plateau in Figure 2.

At shear rates less than τ_{GB} , Newtonian plateau $\eta_N = \text{const}$ is observed at all data sets in Figure 10. In this region, the local break-up rate of the gel structure by shear deformation evidently is comparable to the structural growth or recovery rate due to flocculation, so that the overall resistance to flow is constant. In the intermediate shear stress region (1-3 Pa above τ_{GB}), the rate at which the gel structure is destroyed is greater than the rate of structural growth,

leading to an abrupt decrease in the size of gel domains via fracturing, hence a resulting step-like decrease in viscosity. At shear stresses 10-20 Pa above τ_{GB} and higher, there is a slower reduction in the viscosity which may be attributed to a gradual complete disruption of flocculated domains.

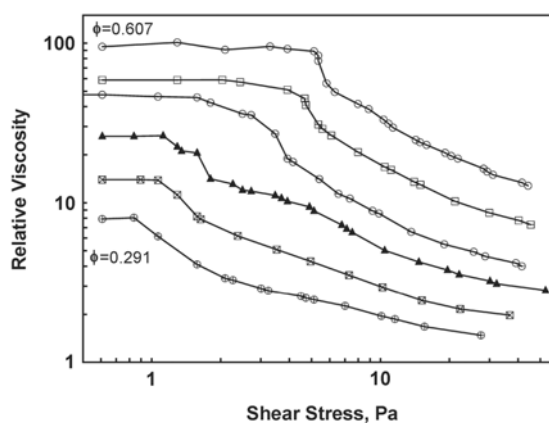


Figure 10. Viscosity vs. stress for emulsions with characteristic gel-break plateau in Figure 2.

In support of the above interpretation, Figure 11 shows ϕ dependencies of relative emulsion viscosities for two constant values of shear stress. For $\tau=0.5$ Pa (at the Newtonian plateau of all data sets in Figure 10), $\eta_{REL}(\phi)$ curve exhibits a prominent viscosity anomaly around $\phi \approx 0.4$, attributed above to the presence of tight emulsion gels. This anomaly is no longer present at $\eta_{REL}(\phi)$ data for $\tau=45$ Pa, the highest shear stress common for all these data sets. Owing to disruption of flocculated gels into a system of individual water droplets, the 45 Pa data may be closely approximated by the above described Mooney model (thick line in Figure 11, $R^2=0.999$). As may be expected, noticeable departure from the smooth Mooney behaviour is observed only for “closely packed” droplet morphologies ($\phi > \phi_{MRJ} \approx 0.64$) and in conditions of free-water separation at $\phi > 0.74$ (cf. discussion of Figure 2).

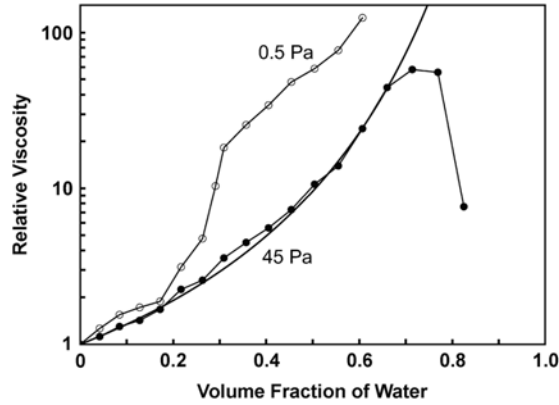


Figure 11. Effects of volume fraction of water in Oil 1 on relative viscosity of W/O emulsions at constant shear stresses of 0.5 Pa (unbroken emulsion gels) and of 45 Pa (disrupted emulsion gels). Thick line – best fit of Mooney approximation for a system of individual water droplets.

Further analysis of the data in Figure 10 reveals a high degree of structural similarity of gel domains in emulsions with $\phi < 0.64$. Namely, all gel-break (shear-thinning) processes commencing at respective $\tau_{GB}(\phi)$ may be described by a single master curve when emulsion viscosity, normalized to the respective value at Newtonian plateau $\eta_{NRM} = \eta/\eta_N$, is plotted against respective “excess shear stress” $\tau_{EX} = \tau - \tau_{GB}$. Figure 11 shows a virtual coincidence of $\eta_{NRM}(\tau_{EX})$ plots for all data sets from Figure 11, except for some deviations near gel-break points.

Universal features of strong shear-thinning due to the gradual break up of flocculated aggregates in emulsions previously have been reported by some authors.^{18-20,31} The master curves of these emulsions were interpreted through various viscosity models of colloidal dispersions, one of the most successful being the Ellis model,⁴³ which in the above terms may be re-written as a two-parameter equation:

$$\eta_{NRM} = \frac{1}{1 + (\tau_{EX} / \tau_c)^{\alpha-1}} \quad (8)$$

The solid line in Figure 11 shows that this Ellis equation provides a good approximation ($R^2=0.954$) of our master curve with the following parameters: $\tau_c = 1.74$ and $\alpha = 1.51$.

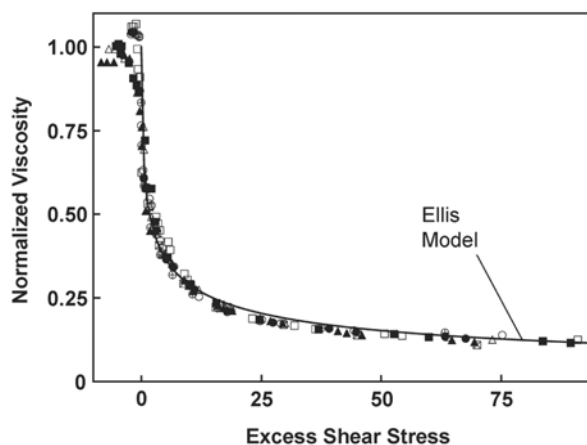


Figure 12. A single master curve for shear-induced break-up of flocculated W/O gels in Oil 1 (cf. the original data sets in Figure 11).

Note that Ellis model is directly related to power-law approximations of flow curves (Eq. 1) with $\alpha-1$ being close to “flow behavior index” n . Hence, the above mentioned “fanning” of high-shear segments of experimental flow curves in Figure 3 may be regarded merely as a consequence of plotting data versus flow parameters originating from zero-shear state. By transferring the origins to respective gel-break points all segments of “destructive flow” should reveal similar power law behavior with $n \approx 0.51$.

4. Summary and Conclusions

Summarizing, flow curves of native petroleum emulsions in concentric-cylinder viscometers are composed of three distinctly different branches.

a. At low-shear ranges, all emulsions with water content below ca. 0.64 exhibit Newtonian behavior. The departure of Newtonian viscosities from theoretical models may be

attributed to the presence of flocculated clusters of water droplets and gel structures, revealed by viscosity anomalies as well as by direct microscopic visualization. In the small-gap viscometer densely-packed clusters are predominant, while in the less constrained large-gap conditions loosely-packed big clusters are also retained. Characteristic tight gels, composed of small droplets are responsible for the largest viscosity anomaly at water volume fractions close to 0.4. As indicated by literature analysis, this viscosity anomaly (and, presumably, the underlying tight gel morphology) may be a universal property of native W/O petroleum emulsions.

As indicated by optical microscopy (cf. Figure 7) once formed, “small-droplet” gel domains apparently retain their structural integrity at higher ϕ , incorporating/stabilizing new portions of water as larger-size droplets. The maximum hold-up of disperse water evidently is the “close packing” limit of $\phi \approx 0.74$. At still higher ϕ additional water readily emerges as a separate phase, hence a characteristic viscosity decrease of emulsions as a consequence of a stratified flow (W/O emulsion gel + free water) - cf. Figures 3 and 11. It should be emphasized that the observed decrease of viscosity was never accompanied by phase inversion of “closely packed” emulsion gel, contrary to the conventional interpretation of viscosity maximum as the reliable indicator of emulsion inversion point.^{36,38,39}

b. At intermediate-shear ranges, gel-break “plateau” appear at flow curves for water contents $\phi \geq 0.142$ in the small-gap viscometer and for $\phi \geq 0.210$ in the large-gap one. Gel-break stress τ_{GB} increases linearly with ϕ , as another indication of the uniformity of emulsion-gel morphologies. Departure from linearity commences above the “maximally random jammed” volume fraction of water droplets $\phi_{MRJ} \approx 0.64$.

c. At high-shear ranges, for $\tau > \tau_{GB}$, shear-induced gel-break processes in all emulsions with $\phi < 0.74$ appear to be identical and may be described by a single master curve in terms of

viscosity, normalized with respect to a gel-break point, versus “excess” shear stress above a gel-break point $\tau_{EX} = \tau - \tau_{GB}$. In turn, this master curve exhibits a good coincidence with predictions of the power-law Ellis model.

In conclusion, the presence of domains with tight, “small-droplet” gel morphology may be a common feature of oil-field W/O native petroleum emulsions. Presently, apparently common mechanisms of gel formation and a common importance of $\phi \approx 0.4$ are not clear. As one of the subjects for further verification we suggest a concept of morphology transformations in the vicinity of “potential” (“suppressed”) phase inversion. For emulsions of simple fluids in the absence of specific surfactants/emulsifiers, inversion (catastrophic) at approximately equal contents of both phases is expected by spatial/thermodynamic considerations.^{44,45} Most frequently, associated structural transformations proceed via small-droplet morphologies accompanying a bicontinuous state.^{46,47} Our suggestion is that in native petroleum emulsions small-droplet structures also start to emerge owing to increasing confinement of disperse phase. However, true inversion is prevented by stabilizing action of indigenous crude oil surfactants which effectively partition into emulsion-gel. These suggestions will be supported in Part II of the present publication by results from optical microscopy, drop size analysis, sedimentation studies and from spectrometry of “oil-in-gel” and “free oil” subphases.

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Morphological Transformations of Native Petroleum Emulsions. I. Viscosity Studies

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