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Excess density in oilfield water—crude oil dispersions

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Abstract

Extensive density measurements were performed with mixtures of 12 degassed (dead) crude oils with respective oilfield brines (formation waters). All unprocessed samples were collected directly from wellheads and contained only indigenous surfactants, such as asphaltenes and fine solids. Nonzero excess densities and excess thermal expansions (evaluated on the assumption of quasi-binary water–oil mixtures) were observed for water cuts in the range from $X = 0.4$ to 0.6 at all studied temperatures $T = 5$–$50\,^{\circ}\mathrm{C}$. We suggest that these results are due to the formation of a dense asphaltene-mediated "middle phase" in the studied w/o dispersions. This suggestion is substantiated by plotting T–X phase diagrams which topologically strongly resemble those conventionally observed in some standard Winsor III-type systems. The formation of a complexly structured "middle phase" has been directly verified by preliminary visual/microscopic studies of a phase separation in a crude oil–water mixture.

Keywords: Crude oil; Brine; Dispersion; Emulsion; Viscosity; Excess density; Middle phase; Bicontinuous phase; Asphaltenes

1. Introduction

The output of a production oil well consists typically of a dispersion of formation water (brine) in a crude oil. Knowledge of the physical properties of water/crude oil dispersions is necessary if the behavior and characteristics of their multiphase flows are to be predicted correctly. These properties are essential for the interpretation of rheological experiments, for development of multiphase metering devices, and for equipment and pipeline design [1–3]. Depending on the water cut and the flow conditions, water/oil dispersions may exhibit transitions among a variety of phase states; in the presence of surfactants, stable emulsions may be formed [4–8]. A well-known type of phase transition in a water/oil mixture is that of a phase inversion from a w/o to an o/w dispersion [1,9–12]. The phase transitions are usually accompanied by noticeable anomalies of some mixture's properties and may be the cause of a significant increase in the pressure gradient in a flowing fluid, of undesirable stability of w/o or o/w emulsions, etc. In spite of extensive research, the microscopic phenomena near the phase transitions are still poorly understood (cf. a recent review [12]). In particular, there is a large diversity of data for oil/brine dispersions from different wellstreams, apparently due to different contents of the "indigenous surfactants" in crude oils, such as asphaltenes, resins, and fine solids [13]. It is suggested that some of these indigenous components may be responsible for specific structural transitions in oilfield w/o mixtures, which precede a phase inversion and resemble the phenomena of formation of "middle phase" microemulsions (Winsor III systems) in model mixtures [12]. Apparently, for oilfield practitioners, dealing with heavy oils and bituminous oilsands, formation of three-phase systems in nonflowing oil–brine mixtures is a well-known phenomenon, the middle (macro)emulsion phase most frequently being referred to as the "rag layer." Although "rag layers" are the cause of costly problems in performance of dewatering/desalting equipment, only recently have these preinversion middle

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phases become objects of systematic experimental investigation [14,15].

Currently, the main method of studying phase transformations in crude oil/water mixtures is that of rheological measurement [1–12,16,17]. It has been repeatedly demonstrated that rheological techniques offer means to determine the inner structure of emulsions and provide evidence of technologically important structural changes. The main drawback of this techniques is the presence of a fluid flow, which may noticeably change the structural properties of an oil/water mixture [1,2,16]. Due to continuous mechanical agitation, flowing dispersions may be dynamically stabilized [18] and may exhibit properties close to those of stable emulsions.

Phase diagrams of nonflowing oil/water mixtures most frequently are investigated by straightforward visualization techniques [19–22]. These techniques are favored owing to their ease of interpretation; however, the volumes of visibly distinct phases cannot be determined with high precision. Moreover, in dark heavy oil or bitumen mixtures some of these phases are visually indistinguishable.

To reveal the details of the phase behavior, it may be useful to apply to a crude oil/brine system, in spite of its compositional complexity, some of the approaches developed for binary liquid–liquid mixtures. Specific molecular interactions in binary mixtures are successfully interpreted on the basis of the Prigogine–Flory–Patterson (PFP) model [23–25], where thermodynamic/interaction parameters are related to measurable macroscopic properties through the so-called excess functions, e.g., the excess molar volume V_m^E. In practice, the values of V_m^E for mixtures of components with well-known molecular weights are calculated from the corresponding density measurements. For such complex components as crude oil and formation water (brine), molecular weights cannot be strictly defined; hence it seems more appropriate to analyze the mixtures not in terms of excess molar volumes but directly in terms of excess densities.

In view of the above arguments, a technique of detailed density measurements (and evaluation of the corresponding excess functions), well developed for simple binary solutions/mixtures, may be applied to studying more complex crude oil/brine mixtures. Though this suggestion may seem trivial, a review of the available (English and Russian language) literature did not reveal any relevant publications. Hence, the present work was aimed at producing new results on density–structure relationships in industrial crude oil–brine mixtures.

2. Experimental

2.1. Samples

The studied crude oil and brine samples were collected from the wellheads at the newly developed Aktanishskoje oil reservoir, Tatarstan, Russia, and have been supplied by the TATNEFT oil company. The basic physicochemical properties of these 12 samples (determined by the supplier) are listed in the upper lines of Table 1. The samples are denoted according to the corresponding productive layers: T—Tulskij; B—Bobrikovskij; K—Kizelovskij. The next two digits denote the individual number of the well, the last two the year of the sampling. It can be seen that according to standard classification schemes (e.g., that of Tissot and Welte [26]), all crudes may be classified as "heavy sour" with densities in the range of ≈897–908 kg/m^3 and sulfur contents above 3 wt%. All brines are strongly mineralized and exhibit densities of 1148–1175 kg/m^3, i.e., salt contents of about 150 g/L, which is somewhat higher than, but close to the values typical for other studies of crude oil/brine mixtures [1]. The bottom line in Table 1 shows the properties of the Romashkinskoje sample, employed in phase separation experiments (cf. Section 3.8).

2.2. Apparatus and procedure

The experimental investigation of oil/brine mixtures has been performed at the TATNIPINEFT Scientific Research

Table 1
Properties of crude oil–brine samples used in density studies (12 upper lines) and in phase separation experiments (bottom line)

Well	Degassed crude oil							Brine
	Density at 20 °C (kg/m^3)	Viscosity at 20 °C (mm^2/s)	MW (g/mol)	Sulfur (wt%)	Asphaltenes (wt%)	Resins (wt%)	Waxes (wt%)	Density at 20 °C (kg/m^3)
T6097	902.2	64.80	250.1	3.68	8.89	19.25	5.59	1153.9
T6098	905.1	69.94	224.3	3.92	3.03	12.65	1.96	1148.2
T6199	904.4	64.34	256.0	4.11	5.13	11.71	3.23	1148.0
B5494	902.4	52.41	250.1	3.30	6.20	11.52	1.42	1174.7
B7695	898.0	49.60	250.1	3.01	7.78	8.60	2.99	1174.7
B0598	897.5	40.93	237.9	3.42	3.85	12.89	2.03	1148.2
B5498	905.4	58.25	246.2	3.29	9.35	10.98	1.86	1148.2
B6698	896.7	42.43	232.5	3.41	3.28	11.45	1.80	1148.2
B4899	904.1	50.72	260.4	4.43	6.04	11.11	12.5	1148.0
B7599	900.5	44.59	277.0	3.32	5.13	11.71	3.23	1152.7
K3396	908.2	66.78	254.1	3.41	4.97	15.60	2.13	1154.9
K4999	906.0	53.10	274.9	3.82	5.35	9.75	12.42	1148.0
Romash	915.0	86.19		2.19	3.29	24.77	2.48	Tap water