



Emulsification of Athabasca bitumen by organic alkali: Emulsion phase behavior and viscosity for bitumen/brine/triethylenetetramine



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ABSTRACT

Recovery of bitumen commonly uses steam assisted-gravity drainage, in which water throughput is intrinsically high. A large amount of condensed water near thermal fronts tends to substantially decrease the effective permeability to bitumen in the conventional gravity drainage process. This research investigates a potential way to use the condensed-water phase as an effective carrier for bitumen by making oil-in-water (o/w) emulsion. The expected mechanism depends on emulsification of bitumen into the water phase by natural surfactants that are generated through reactions of acidic oil components with organic alkali.

The main objective of this paper is to study the ability of an organic alkali to create o/w emulsions that are much more mobile than the original bitumen. Triethylenetetramine (TETA) was selected as organic alkali for this paper with no other additives. The main contribution of this paper is a new set of experimental data (phase behavior and viscosities) for emulsions for mixtures of Athabasca bitumen, TETA, and NaCl brine at a wide range of alkali concentrations, salinities, and water-to-oil ratios (WORs) at temperatures up to 373 K.

Results show that the o/w emulsions created by TETA can be an effective bitumen carrier with a low viscosity and high bitumen content in the emulsion. It is possible to create o/w emulsions by adding a small amount of TETA to Athabasca bitumen and NaCl brine. Single-phase o/w emulsions, which are desirable as a bitumen carrier, were observed for TETA concentrations below 5.0 wt% at salinities 0 ppm and 1000 ppm at 373 K. The bitumen content in o/w emulsion was the highest for 2.0 wt% TETA samples, and it increased with increasing temperature. In comparison to the original bitumen, o/w emulsions were 4–5 orders of magnitude less viscous at 298 K, 2 to 3 orders of magnitude less viscous at 323 K, and 1 to 2 orders of magnitude less viscous at 353 K.

1. Introduction

Steam injection is the most widely used method of bitumen recovery, which uses the sensitivity of bitumen viscosity to temperature. Steam injection processes, such as cyclic steam stimulation (CSS) and steam assisted gravity drainage (SAGD), are energy-intensive, using water as a heat carrier. Water throughput is intrinsically high in these steam-based oil recovery methods. For example, a cumulative steam-to-oil ratio (SOR) is between 2 and 5 in successful SAGD for relatively homogeneous reservoirs (Butler, 2001). Cumulative SOR tends to increase for more heterogeneous reservoirs (Venkatramani and Okuno, 2017). Therefore, it is important to consider how the water component and/or the aqueous phase can be used to improve the efficiency of steam-based oil recovery methods. For the conventional steam injection processes, however, the condensed water phase is not utilized for the purpose of in-situ bitumen transport. Rather, the presence of the water

phase adversely affects the oleic-phase mobility by reducing the phase relative permeability (Sharma and Gates, 2010; Shi and Okuno, 2018).

The central question that motivated the current research is whether it is possible to increase the efficiency of bitumen transport by making oil-in-water (o/w) emulsion, in which the water-continuous emulsion acts as an effective carrier of bitumen. A potential way to make o/w emulsions in steam injection is to coinject organic alkali with steam.

Organic alkalis create a high-pH solution (e.g., pH higher than 10) when mixed with liquid water, which is abundant near the edge of a steam chamber. Then, the water phase with high pH is expected to activate naphthenic acids as natural surfactants, which are commonly present in heavy oil and bitumen. Bitumen can be emulsified with in-situ natural surfactants created by the reaction of alkali with acidic components in the bitumen. In addition, the stability of bitumen emulsions can be enhanced by asphaltenes and resins, which are present at high concentrations in bitumen. It has been found that the

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interactions of water with asphaltenes and resins are conducive to creating stable emulsions (Kar et al., 2014; Yan et al., 1999; Yarranton et al., 2000; Xia et al., 2004; Kokal, 2005; Gao et al., 2017; Jia and Okuno, 2017). The relative amounts of asphaltenes and resins in oil are also an important factor for emulsion properties (Al-Sahhaf et al., 2008; Schorling et al., 1999; Yang et al., 2007). Depending on the phase behavior, how in-situ surfactants act varies. However, steam-based recovery methods usually yield low-salinity conditions near thermal fronts, where steam condensate makes high water saturations. At low-salinity conditions (e.g., 1000 ppm), in-situ surfactants tend to create o/w emulsion, which transports bitumen by the fast-flowing aqueous phase.

Emulsification of heavy oil has been studied for different purposes. For heavy oil recovery, alkali injection was investigated in water flooding processes, such as alkaline-surfactant, alkaline-surfactant-polymer, and alkaline-co-solvent-polymer flooding (Bryan and Kantzas, 2007a,b; Bryan et al., 2008; Dong et al., 2009; Fortenberry et al., 2015; Kumar et al., 2012; Liu et al., 2006, 2007; Pei et al., 2013; Xiao et al., 2017; Zhang et al., 2016). In these studies, different combinations of alkalis, salts, surfactants, co-solvents and polymers were tested to achieve ultra-low interfacial tension and low viscosity. O/w emulsion for pipeline transportation has been studied by testing emulsion viscosity at different surfactants, alkalis and solvents with different WORs and shear rates (Abdurahman et al., 2012; Ashrafizadeh and Kamran, 2010; Ashrafizadeh et al., 2012; Hasan et al., 2010; Ghannam et al., 2012; Ghannam and Esmail, 2007).

Synthetic surfactants have been studied as steam additives for SAGD and CSS (Lu et al., 2017; Srivastava and Castro, 2011; Zeidani and Gupta, 2013). They used commercially available hydrophilic viscosity reducers (Lu et al., 2017), hydrophilic surfactants (Zeidani and Gupta, 2013), and thin film spreading agents (Srivastava and Castro, 2011) to create oil-in-water (o/w) emulsions or to demulsify water-in-oil (w/o) emulsion to enhance bitumen transport. The potential mechanisms for lowering SOR by injecting these surfactants with steam include the wettability alteration from oil-wetting to more water-wetting, and reduction of interfacial tension.

O/w emulsification of heavy oil by natural surfactants was studied using inorganic alkalis (Acevedo et al., 2001; Ashrafizadeh et al., 2012). With no other surfactants or solvents, they used sodium carbonate (Na_2CO_3) to create natural surfactants and o/w emulsion from Iranian heavy crude oil (Ashrafizadeh et al., 2012) and Cerro Negro bitumen (Acevedo et al., 2001). In both studies, o/w emulsions were observed at sodium carbonate concentration range of 2000 to 10,000 ppm. However, Cerro Negro bitumen created more stable o/w than the other.

For bitumen recovery using o/w emulsions, Kim et al. (2017) studied on alkali-steam coinjection for SAGD. They injected steam with alkali (not specified) into a micromodel chip and achieved significant improvement in oil recovery by creating o/w emulsions. Although the size of emulsion droplets was measured, Kim et al. (2017) did not study phase behavior and rheology of emulsions created in their experiment.

This paper presents an experimental study of potential advantages of using organic alkali as an additive for steam injection. An organic alkali can induce o/w emulsions by reaction with acidic components in bitumen and activating natural surfactants with no other chemicals, such as synthetic surfactants and cosolvents. The optimal conditions to create o/w emulsions depend on many variables such as alkali concentrations, brine salinities, temperatures, and WORs. It is important to obtain fundamental experimental data for emulsion phase behavior and viscosity of mixtures of Athabasca bitumen, brine, and organic alkali. The main objectives of this research are to:

- 1) Investigate whether o/w emulsions can be created by adding organic alkali to Athabasca bitumen and NaCl brine
- 2) Obtain phase behavior data for bitumen emulsification by natural surfactants activated with different alkali concentrations, WORs, brine salinities, and temperatures

- 3) Measure the oil content in o/w emulsions to confirm the o/w emulsion is an effective bitumen carrier in the water-continuous phase
- 4) Measure the viscosity of o/w emulsions and compare how much viscosity reduction can be achieved by creating o/w emulsions

Triethylenetetramine or TETA is used for this paper, as part of the initial stage of our research on bitumen emulsification by organic alkali. TETA is not a new compound to reservoir processes, as it is sometimes used as cosolvent in surfactant flooding. Also, use of TETA allows us to study high-temperature phase behavior in a safe manner because of its high boiling temperature.

Section 2 describes materials and experimental procedures employed in this research. Then, results are presented and discussed in Section 3. Finally, Section 4 gives key conclusions of this research.

2. Materials and methods

2.1. Materials

The molecular weight (MW), density and SARA of the Athabasca bitumen sample used in this research were measured by Exova laboratory (Edmonton, Alberta, Canada). The molecular weight (MW) was measured to be 532 g/mol by the freezing point depression method. The density was measured to be 0.985 g/ml at 335 K and atmospheric pressure by ASTM 7042-12a. The SARA analysis showed the following composition: 24.5 wt% saturates, 36.6 wt% aromatics, 21.1 wt% resins, and 17.8 wt% asphaltenes (pentane insoluble). For more information about this bitumen, Baek et al. (2017) presented viscosities and densities of this bitumen sample at temperatures from 316 to 451 K and pressures from 1.6 to 100 bars.

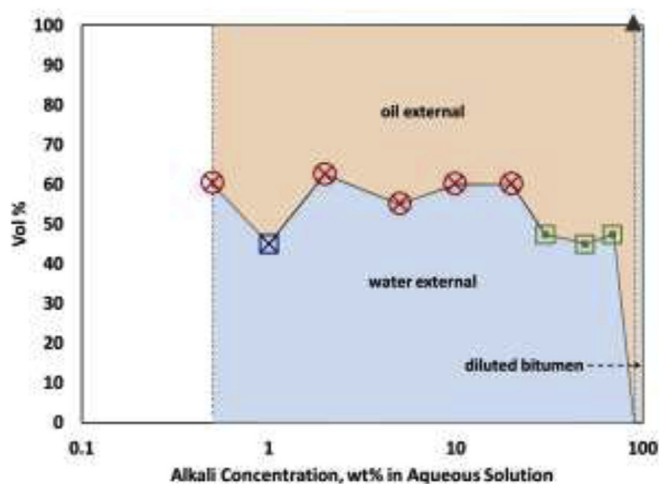
The total acid number was measured to be 3.56 mg-KOH/g-oil by using the method of Fan and Buckley (2007). Cooke et al. (1974) stated that the acid number of oil required for an alkali-based method was 1.5 mg KOH/g-oil. In their sandpack flooding experiment, Ge et al. (2012) showed that a higher acid number resulted in a higher oil recovery among their four oil samples with acid numbers between 1.85 and 4.66. Therefore, the acid number of the bitumen sample, 3.56 mg-KOH/g-oil, indicates that the bitumen contains a sufficient amount of acidic components to create natural surfactants by adding organic alkali.

For aqueous solutions, brines with different salinities were prepared with deionized water and NaCl. TETA makes a high pH aqueous solution. For example, pH values were measured to be between 10.2 and 11.4 for 1000 ppm NaCl brine with 10 different TETA concentrations, 0.5, 1.0, 2.0, 5.0, 10.0, 20.0, 30.0, 50.0, 70.0, and 90.0 wt%. Sheng (2015) indicated that a high pH in the aqueous solution is favorable for creating natural surfactants by the reactions of alkali with acid components in bitumen.

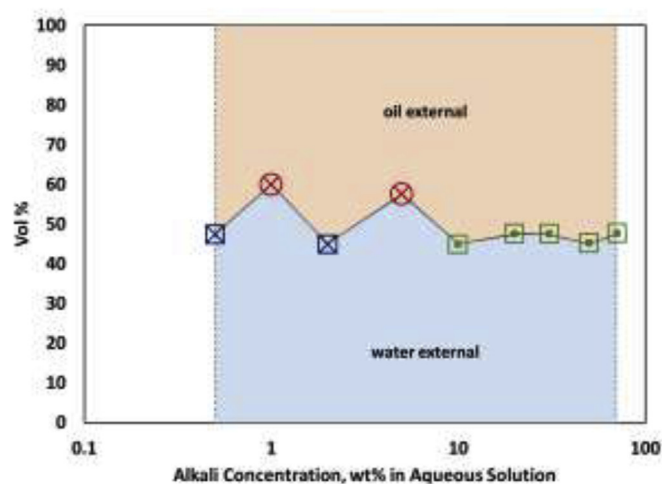
TETA has a chemical formula, $\text{C}_6\text{H}_{18}\text{N}_4$, and a molecular weight of 146 g/mol. TETA was selected for the current paper, considering experimental safety and convenience in the initial stage of the research on bitumen emulsification; i.e., TETA's high boiling point (551 K) makes it safer and easier to study emulsion properties at high temperatures. TETA is sometimes used as cosolvent for surfactant injection processes. That is, TETA not only increases pH to make natural surfactants, but also is expected to act as cosolvent in the emulsions created in this research.

2.2. Emulsion preparation

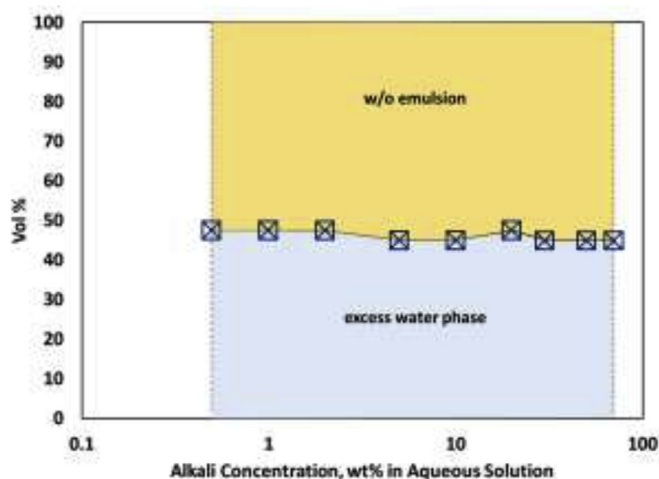
Emulsion phase behavior was studied at different TETA concentrations, salinities, WORs, and temperatures at atmospheric pressure. Since there are many experimental variables that affect bitumen emulsification, the study was conducted in two steps: general phase behavior scans followed by more detailed analysis of specific samples.



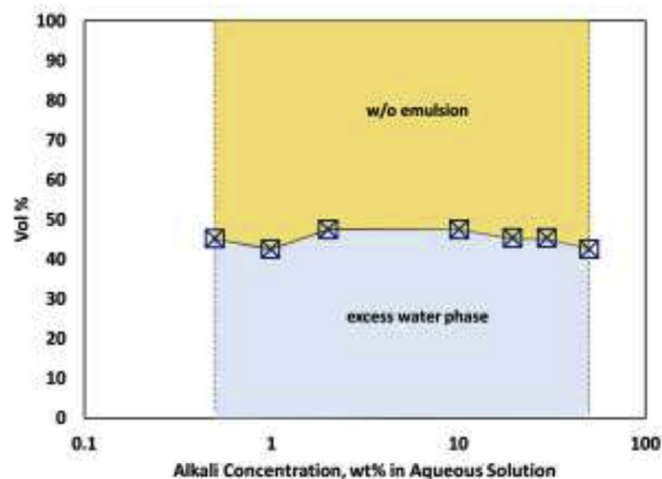
a. Salinity 0 ppm



b. Salinity 1,000 ppm



c. Salinity 30,000 ppm



d. Salinity 100,000 ppm

Fig. 1. (Section 3-1). Emulsion phase behavior at the water-oil-ratio (WOR) of 5:5 after aging at 373 K for 3 weeks; a. 0 ppm, b. 1000 ppm, c. 30,000 ppm, and d. 100,000 ppm. At 0 ppm, o/w emulsions with excess oil phase were observed at 1.0 wt% and 5.0 wt%. Other than those points, w/o emulsion (bitumen rich) with o/w emulsions (water-rich) were observed at 0 ppm and 1000 ppm. For 30,000 ppm and 100,000 ppm, all samples showed w/o emulsions with excess water phase.

- ⊗ : oil-in-water emulsions with excess oil phase.
- ◻ : water-in-oil emulsions (bitumen rich) with oil-in-water emulsions (water rich).
- ⊠ : water-in-oil emulsions with excess water phase.
- ▲ : diluted bitumen.

The purpose of the general scan is to observe bitumen emulsification at a broad range of conditions, and to identify conditions conducive to o/w emulsions.

At the first stage, samples were prepared at 10 different alkali concentrations (0.5, 1.0, 2.0, 5.0, 10.0, 20.0, 30.0, 50.0, 70.0, and 90.0 wt% in aqueous phase) with 4 different salinities (0 ppm, 1000 ppm, 30,000 ppm, and 100,000 ppm) for 3 different WORs (5:5, 7:3, and 9:1). However, NaCl did not completely dissolve in water at sample conditions of 30,000 ppm for 90.0 wt% TETA and 100,000 ppm for 70.0 wt% and 90.0 wt% TETA. Also, three samples were lost due to mechanical failures of glass pipettes. As a result, the general phase behavior study was conducted for a total of 108 samples at 373 K.

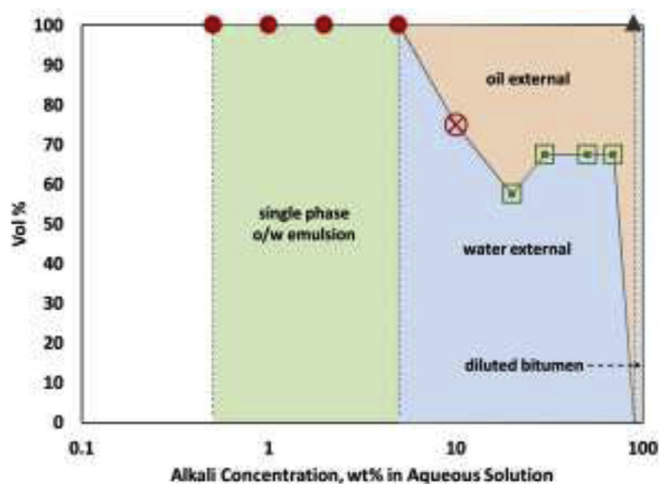
Measured pH values indicated that all acidic components were reacted with TETA for all samples. For instance, the minimum pH measured was 9.7 for the sample of 0.5 wt% TETA at WOR 5:5.

For each sample, 4-ml sample was prepared in 10-ml Pyrex pipette

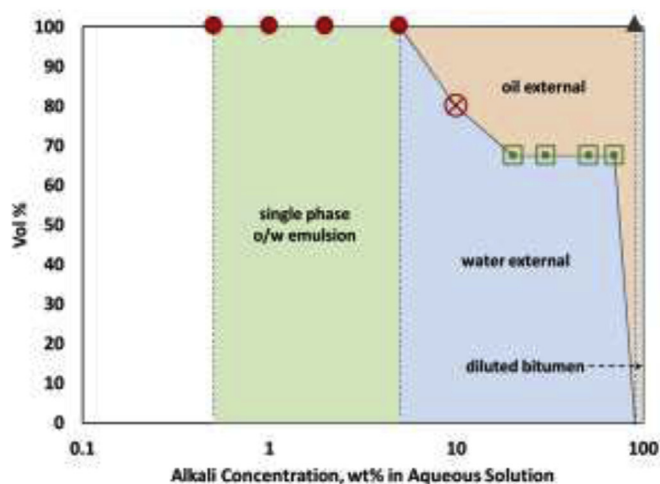
as follows. First, the tip of a pipette was sealed by flame. Then, specified amounts of brine, TETA, and bitumen were added in this order into the pipette. The bitumen was heated up to 353 K before the injection to make it more mobile. After injecting all components, argon gas was injected into the pipette as a blanket gas. Finally, the neck of the pipette was sealed by flame. The samples were aged in an oven at 373 K for a certain time period; e.g., 3 weeks for this general scanning. During the aging period, samples were mixed 4 times a day. Then, samples were rested for 2 days before reporting emulsion phase behavior at 373 K.

After the general scans, samples with 5 alkali concentrations (0.5, 2.0, 5.0, 50.0 and 90.0 wt% in aqueous phase) at 1000 ppm at WOR 7:3 were chosen for more specific analysis. This WOR corresponds to a typical SOR in CSS and SAGD. The selected salinity is also within a typical range of salinities of produced water in these steam-based oil recovery methods.

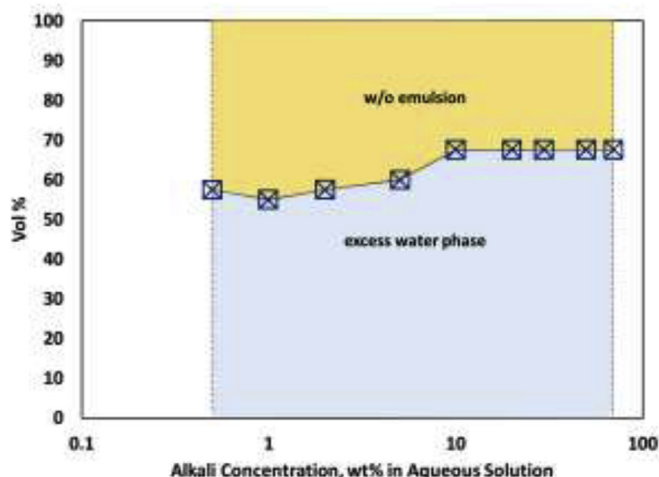
For the second stage of specific analysis, 8-ml sample was prepared



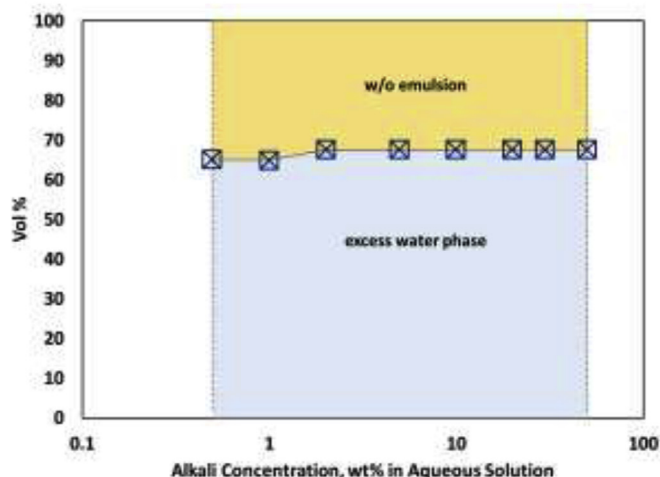
a. Salinity 0 ppm



b. Salinity 1,000 ppm



c. Salinity 30,000 ppm



d. Salinity 100,000 ppm

Fig. 2. (Section 3-1). Emulsion phase behavior at the water-oil-ratio (WOR) of 7:3 after aging at 373 K for 3 weeks; a. 0 ppm, b. 1000 ppm, c. 30,000 ppm, and d. 100,000 ppm. Single-phase o/w emulsions were observed up to 5.0 wt% at 0 ppm and 1000 ppm. At 10.0 wt%, o/w emulsions with excess oil phase were observed at 0 ppm and 1000 ppm. From 20.0 wt%, w/o emulsion (bitumen rich) with o/w emulsions (water-rich) were observed at 0 ppm and 1000 ppm. For 30,000 ppm and 100,000 ppm, all samples showed w/o emulsions with excess water phase.

- : a single phase oil-in-water emulsion.
- ⊗ : oil-in-water emulsions with excess oil phase.
- ▣ : water-in-oil emulsions (bitumen-rich) with oil-in-water emulsions (water-rich).
- ⊠ : water-in-oil emulsions with excess water phase.
- ▲ : diluted bitumen.

in a 10-ml Pyrex pipette by following the same preparation procedure as in the general scanning stage. These specific samples were observed at 4 different temperatures (298 K, 323 K, 353 K, and 373 K) and 3 different aging times (1 week, 2 weeks, and 3 weeks).

2.3. Emulsion type and bitumen content

Identification of emulsion types, water-external and oil-external, was based on visual observation, emulsion volume, emulsion mobility, and the method used in Kumar et al. (2012). Kumar et al. (2012) identified emulsion types by putting emulsion droplets into deionized water and toluene. They observed that o/w emulsion droplets spread in deionized water, but not in toluene. Behavior of w/o emulsions, in which oil is the external phase, was observed in the opposite way.

The amount of bitumen in o/w emulsions was measured by separating oil from water by adding HCl for demulsification. For 1 ml of o/w

emulsion, 2 ml of 3.5 molarity HCl solution was added to make a total solution of 3 ml. This mixture of emulsion and HCl was stirred until transparent water was separated from bitumen. Then, the volume of bitumen was obtained by measuring the volume of separated water.

2.4. Emulsion viscosity measurement

Emulsion viscosities were measured for the samples with a salinity of 1000 ppm and WOR of 7:3 at 5 different TETA concentrations 0.5, 2.0, 5.0, 50.0, and 90.0 wt% in aqueous solution. A specific phase sample was taken from the pipette prepared. Then, its viscosities were measured at 298 K, 323 K and 353 K. Viscosity measurements at higher temperatures were not conducted because vaporization of light components could be substantial.

A rheometer (Model: ARES LS-1 from TA Instruments) was used with 50-mm diameter parallel bottom and upper plates. For each

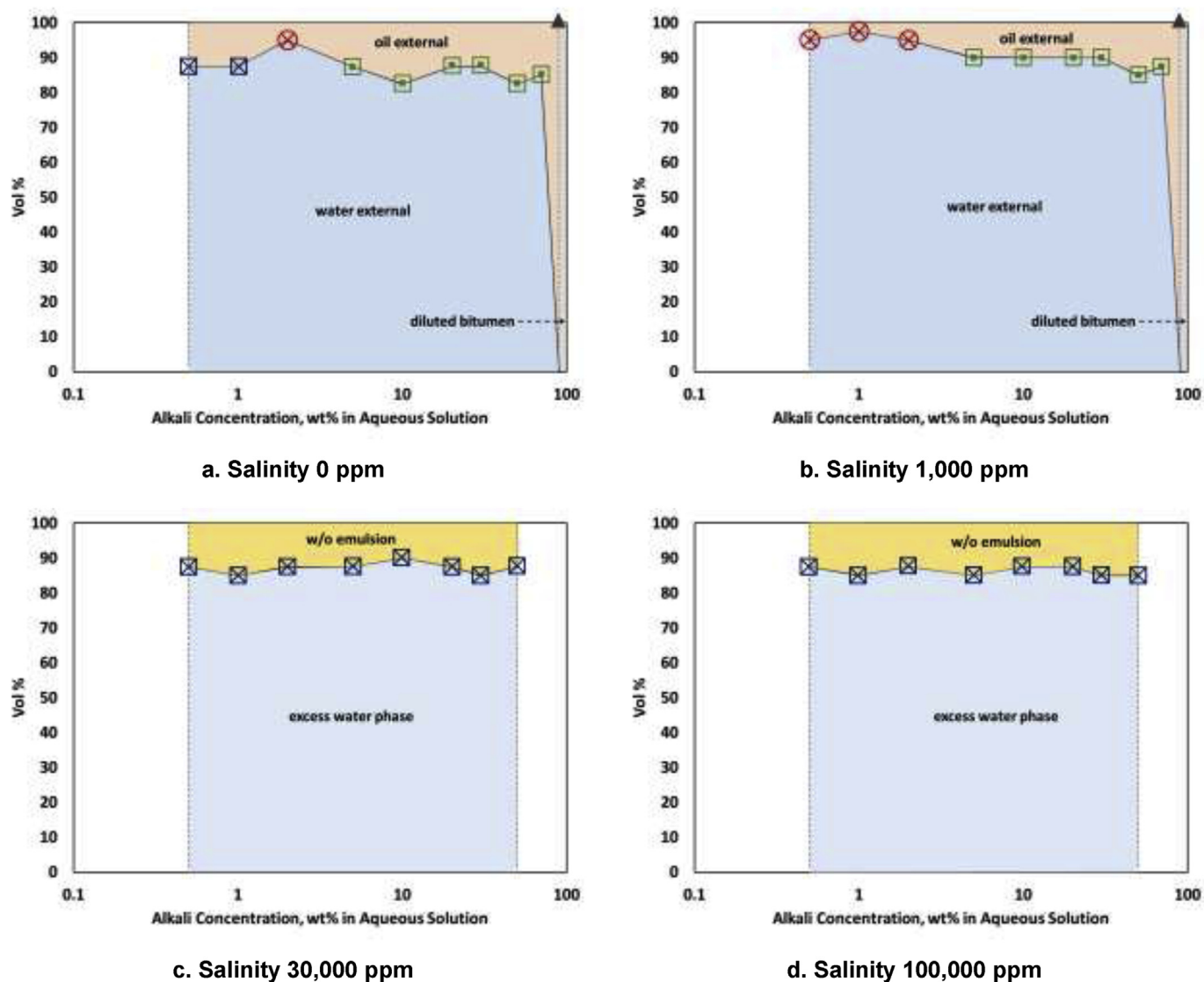


Fig. 3. (Section 3-1). Emulsion phase behavior at the water-oil-ratio (WOR) of 9:1 after aging at 373 K for 3 weeks; a. 0 ppm, b. 1000 ppm, c. 30,000 ppm, and d. 100,000 ppm. At 0 ppm, w/o emulsions with excess water phase were observed at 0.5 wt% and 1.0 wt%. At 2.0 wt%, o/w emulsions with excess oil phase were observed. From 5.0 wt%, w/o emulsion (bitumen rich) with o/w emulsions (water-rich) were observed up to 2.0 wt%. From 5.0 wt%, w/o emulsion (bitumen rich) with o/w emulsions (water-rich) were observed. For 1000 ppm, o/w emulsions with excess oil phase were observed. For 30,000 ppm and 100,000 ppm, all samples showed w/o emulsions with excess water phase.

● : oil-in-water emulsions with excess oil phase.
 ■ : water-in-oil emulsions (bitumen-rich) with oil-in-water emulsions (water-rich).
 ■ : water-in-oil emulsions with excess water phase.
 ▲ : diluted bitumen.

measurement, an emulsion sample taken from a pipette was transferred on the bottom parallel plate of the rheometer. Different gap sizes were selected for different viscosity ranges by considering the maximum torque of this rheometer. The gap size was set to 0.4 mm for o/w emulsions, and 0.8 mm for w/o emulsions. The range of shear rates was from 0.1 to 100 sec^{-1} in this research. The lower limit of torque during viscosity measurement was set to 0.74 μNm because measurements with lower torques might not be reliable. For each emulsion sample, viscosity was measured 2–4 times. The average value for the viscosities measured for each emulsion sample is presented in this paper.

Special care was taken to avoid any possible errors in viscosity measurement using this particular rheometer as described in Tagavifar et al. (2017). For each measurement, a new sample was loaded to prevent any alteration of emulsion rheology through experiencing high shear rates. Although it is ideal to measure viscosity right after loading of a sample, samples were placed on the rheometer for several minutes

for viscosity measurement at 323 K and 353 K to reach the target temperature.

3. Results and discussion

3.1. Emulsion phase behavior

The general phase behavior test was based on 108 samples as described in section 2.2. Figs. 1–3 summarizes the observed phase behavior. Emulsion types and volume fractions were identified by using the method described in section 2.3. For these figures, 3 main types of phase behavior were observed: (1) a single-phase emulsion, (2) two emulsion phases, and (3) diluted bitumen with TETA. The first type, a single-phase emulsion, was o/w emulsion. The two coexisting emulsion phases consisted of the water-external and oil-external emulsions. However, different levels of solubilization in emulsion (oil in water and

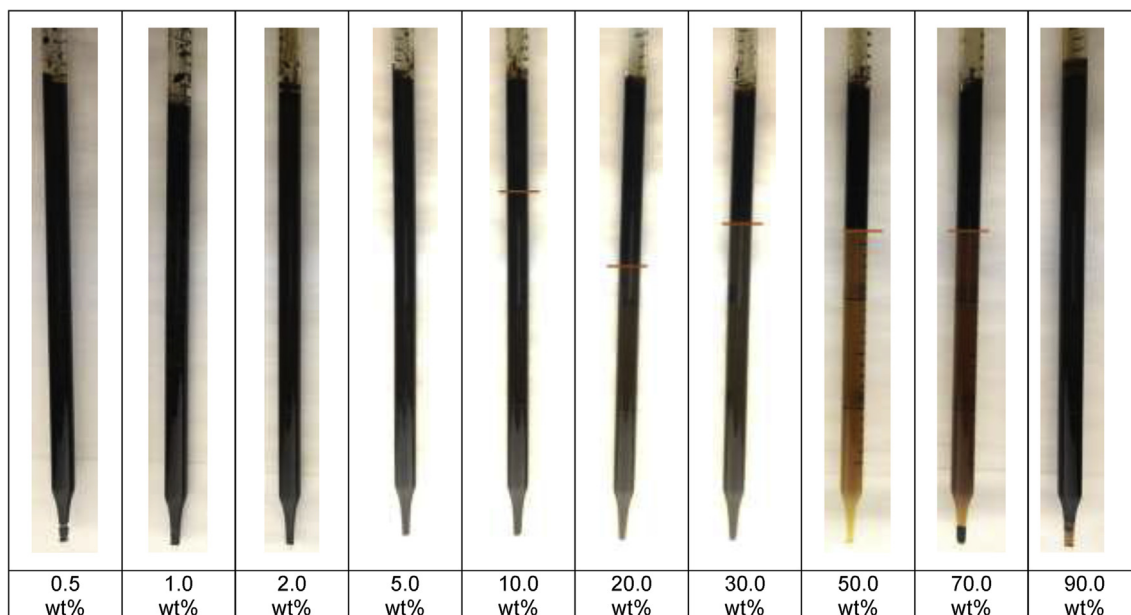


Fig. 4. (Section 3-1). Emulsion phase behavior at different TETA concentrations with zero salinity and water-oil-ratio (WOR) of 7:3, after aging at 373 K for 3 weeks. From 0.5 wt% to 5.0 wt%, a single-phase o/w emulsion was created. o/w emulsions with an excess oil phase were observed at 10.0 wt%. From 20.0 wt% to 70.0 wt%, w/o emulsions (bitumen-rich) with o/w emulsion (water-rich) were observed.

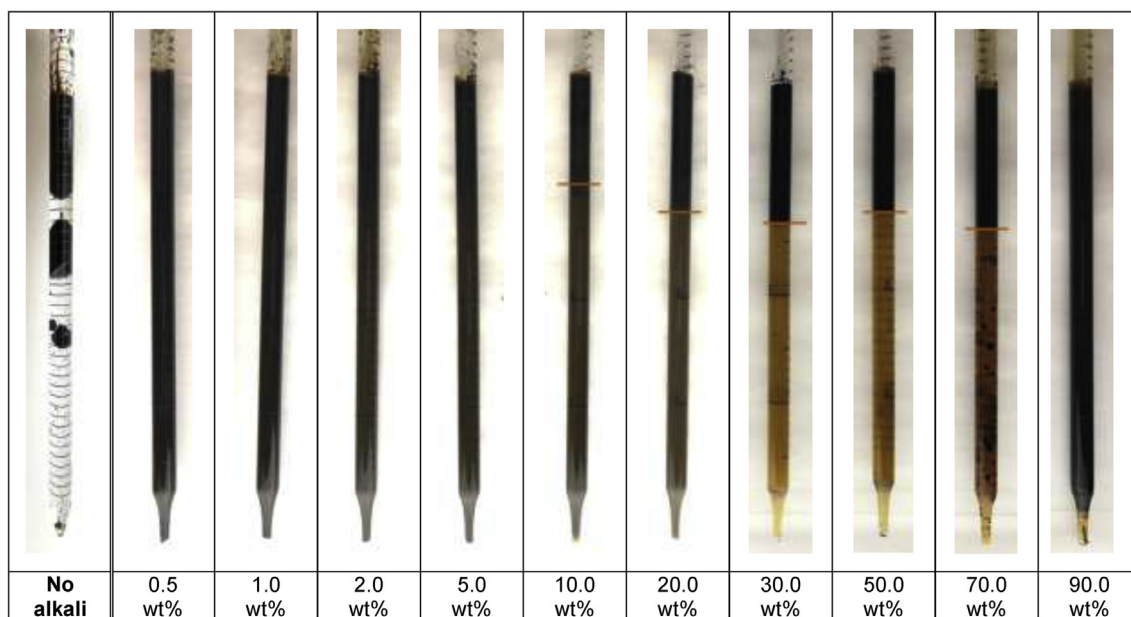


Fig. 5. (Section 3-1). Emulsion phase behavior at different TETA concentrations with 1000 ppm salinity and water-oil-ratio (WOR) of 7:3, after aging at 373 K for 3 weeks. From 0.5 wt% to 5.0 wt%, a single-phase o/w emulsion was created. o/w emulsions with an excess oil phase were observed at 10.0 wt%. From 20.0 wt% to 70.0 wt%, w/o emulsions (bitumen-rich) with o/w emulsion (water-rich) were observed. The effect of alkali on bitumen emulsification is clearly shown in comparison to the no-alkali case.

water in oil) made it possible to observe three sub-types: (2a) o/w emulsion with an excess oil phase, (2b) bitumen-rich w/o emulsion with water-rich o/w emulsion, and (2c) w/o emulsion with an excess-water phase. The third type of phase behavior was observed only for 90.0 wt% TETA samples, which was amine-diluted bitumen.

General observations based on these figures are as follows: First, o/w emulsions tend to occur at low TETA concentrations (< 10.0 wt%) and low NaCl salinities (< 1000 ppm). As TETA concentration increase, w/o emulsions appeared. A diluted bitumen was observed to be a single phase at the highest TETA concentration studied, 90.0 wt%.

Second, a single-phase o/w emulsion was observed for WOR of 7:3,

salinities of 0 ppm and 1000 ppm, and TETA concentrations from 0.5 wt% to 5.0 wt% (Fig. 2). These single-phase emulsions were considered to be optimal phase behavior for the next stage of specific sample analysis as will be discussed later.

Third, at WOR of 9:1 (Fig. 3), o/w emulsions were lean in bitumen owing to a small amount of natural surfactants in the sample. The amount of natural surfactants in water was also reduced at high salinity conditions, 30,000 ppm and 100,000 ppm, causing only w/o emulsions with a transparent water phase.

In general, the inversion of emulsion types was observed in two ways; o/w emulsions were converted into w/o emulsions with

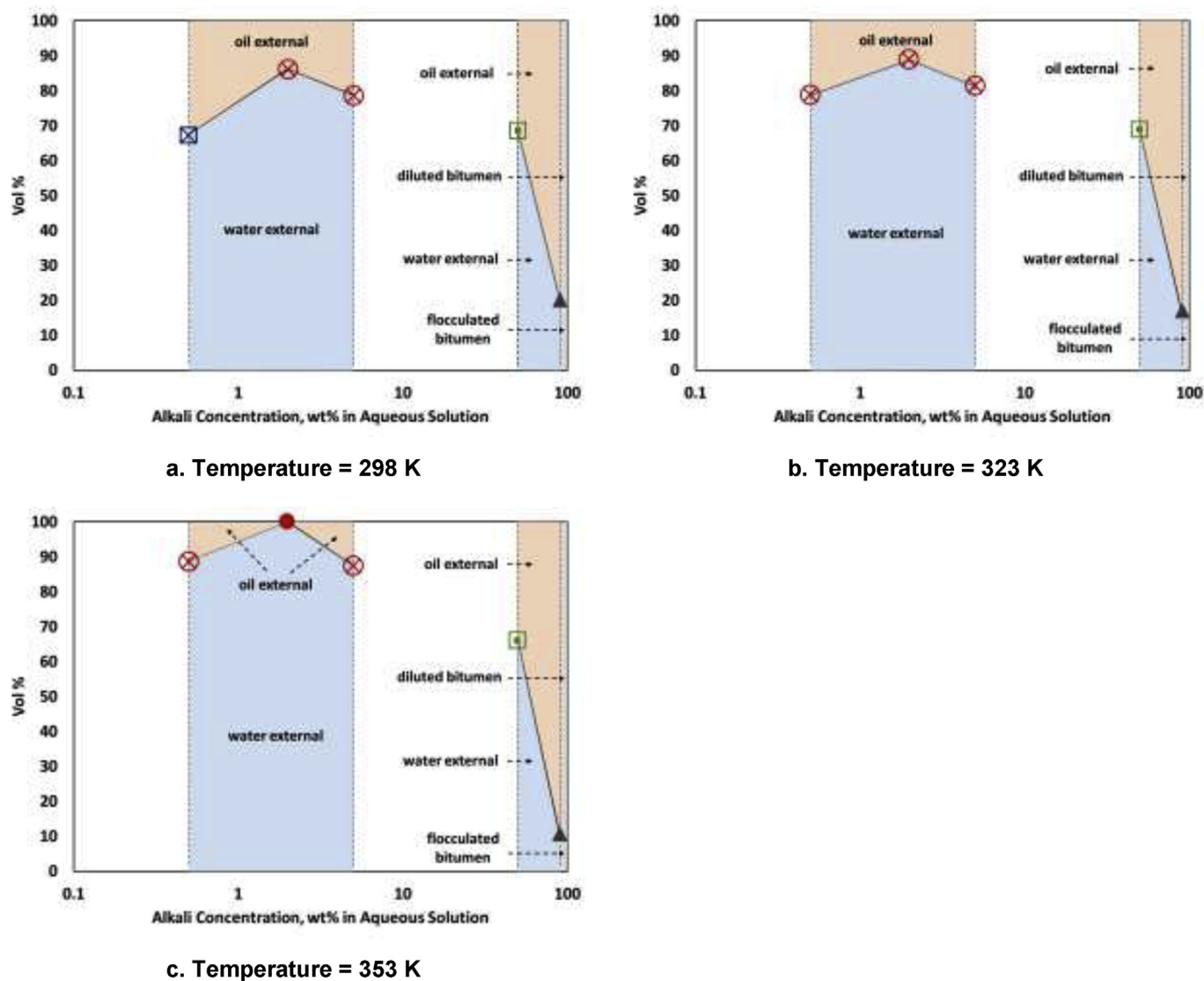


Fig. 6. (Section 3-1). Phase Behavior of emulsions at 298 K, 323 K, and 353 K. Other conditions are fixed at water-oil-ratio (WOR) of 7:3, 1000 ppm and aging for 3 weeks. At 298 K, w/o emulsions with excess water phase was observed at 0.5 wt% and o/w emulsions with excess oil phase were observed at 2.0 wt% and 5.0 wt%. At 323 K, o/w emulsions with excess oil phase were observed at 0.5 wt%, 2.0 wt% and 5.0 wt%. At 353 K, single phase o/w emulsions were observed only at 2.0 wt% and o/w emulsions with excess oil phase were observed at 0.5 wt% and 5.0 wt%. For 5.0 wt% TETA samples, the location o/w emulsions were changed from bottom to top as temperature increased from 298 K to 323 K and it was remained on the top at 353 K. For 90.0 wt% at all temperatures, inhomogenously diluted bitumen resulted in a small amount of flocculated bitumen at the bottom.

- : a single phase oil-in-water emulsion.
- ⊗ : oil-in-water emulsions with excess oil phase.
- ◻ : water-in-oil emulsions (bitumen-rich) with oil-in-water emulsions (water-rich).
- ▲ : diluted bitumen.

increasing TETA concentration or with increasing salinity. The overall effect of alkali concentration, NaCl concentration, and WOR on the phase behavior of bitumen emulsification indicated that the conditions conducive to creating o/w emulsions are low alkali concentrations and salinities below 1000 ppm. Figs. 4 and 5 show phase behavior observed at WOR 7:3 and 373 K. A single-phase o/w emulsion can be seen from 0.5 wt% to 5.0 wt% of TETA in aqueous phase at 0 ppm (Fig. 4) and 1000 ppm (Fig. 5). As a reference, Fig. 5 shows the mixture of bitumen and brine (1000 ppm) with no alkali at WOR 7:3 and 373 K. The effect of alkali on bitumen emulsification can be clearly compared with this no-alkali sample.

Based on the general phase behavior test, 5 TETA concentrations (0.5, 2.0, 5.0, 50.0 and 90.0 wt%) at 1000 ppm and WOR 7:3 were selected for further experiments, such as the effect of temperature, emulsion viscosity, and the bitumen content in emulsion. Phase

behavior at 298 K, 323K and 353 K is summarized in Fig. 6, which can be compared with Fig. 2b at 373 K. Comparisons between Figs. 2b and 6 indicate that higher temperature is more favorable to create a single-phase o/w emulsion with TETA.

3.2. Bitumen content and viscosity of oil-in-water emulsions

This section presents measurements of bitumen content and viscosity of emulsion samples at 1000 ppm and WOR 7:3 at 298 K, 323 K, and 353 K. Phase behavior for these samples was presented in Fig. 6.

Table 1 summarizes measured bitumen contents in emulsions for those samples after 3 weeks of aging. Although the bitumen contents in emulsions were also measured for samples with shorter periods of aging, 1 week and 2 weeks, the effect of aging time was not observed. That is, the emulsions were kinetically stable after 1 week.

Table 1

(Section 3-2). The amount of bitumen in oil-in-water emulsions at 1000 ppm and water-oil-ratio (WOR) of 7:3 after aging for 3 weeks. The amount of bitumen is 2.4 ml in the total of 8 ml of each sample. Samples with 2.0 wt% TETA show the highest concentration of bitumen in o/w emulsions for all temperatures.

a. Temperature = 298 K						
TETA Concentration [wt%]	Emulsion Type	Emulsion Volume [ml]	Volumetric Composition of Emulsion			
			Oil		Brine	
			[ml]	[%]	[ml]	[%]
0.5	w/o	2.6	2.4	92.3	0.2	7.7
2.0	o/w	6.9	1.3	18.8	5.6	81.2
5.0	o/w	6.3	0.7	11.1	5.6	88.9
b. Temperature = 323 K						
TETA Concentration [wt%]	Emulsion Type	Emulsion Volume [ml]	Volumetric Composition of Emulsion			
			Oil		Brine	
			[ml]	[%]	[ml]	[%]
0.5	o/w	6.3	0.7	11.1	5.6	88.9
2.0	o/w	7.1	1.5	21.1	5.6	78.9
5.0	o/w	6.5	0.9	13.8	5.6	86.2
c. Temperature = 353 K						
TETA Concentration [wt%]	Emulsion Type	Emulsion Volume [ml]	Volumetric Composition of Emulsion			
			Oil		Brine	
			[ml]	[%]	[ml]	[%]
0.5	o/w	7.1	1.5	21.1	5.6	78.9
2.0	o/w	8.0	2.4	30.0	5.6	70.0
5.0	o/w	7.0	1.4	20.0	5.6	80.0

Table 1 shows that the o/w emulsion at 2.0 wt% TETA showed the highest concentration of bitumen among the three TETA concentrations compared here. Also, the bitumen concentration in emulsion tends to increase with increasing temperature. As a result, the o/w emulsion at 2.0 wt% TETA at 353 K is a single phase containing all the bitumen (as confirmed in Fig. 6c).

Emulsion viscosities were measured for samples with alkali concentrations of 0.5, 2.0, 5.0, 50 and 90.0 wt% at 298 K, 323 K and 353 K after 3 weeks of aging at 373 K. Viscosity measurement was focused on the oil-rich phase for each sample, including o/w emulsions for which the bitumen content was reported in Table 1. For 0.5 wt% TETA at 298 K, however, the excess-water phase was present with w/o emulsion. For this sample, viscosity measurement was conducted for w/o emulsion, instead of the water-rich excess phase. Also, viscosity measurement was conducted for w/o emulsion for 50.0 wt% TETA since it was the oil-rich phase as can be seen in Fig. 5.

Table 2 presents the measured viscosities, all of which show shear thinning behavior. O/w emulsions are 2.0–5.0 wt% TETA at 298 K, 0.5–5.0 wt% TETA at 323 K, and 0.5–5.0 wt% at 353 K, and they are clearly less viscous than oil-continuous phases. The shear-thinning behavior indicates hydrodynamic interaction and deformation of dispersed droplets (Pal, 1996; Nizamidin et al., 2015). However, the w/o emulsions created in this research showed weaker shear-thinning behavior because there was only a small amount of dispersed water in these oil-external emulsions (Pal, 2000).

Fig. 7 shows measured viscosities for three shear rates, 1.0, 5.6 and 10.0 sec^{-1} , which are relevant to rheological conditions in reservoir flow. There are three types of fluids in this figure: o/w emulsions at TETA concentrations of 0.5 wt% (at 323 K and 353 K), 2.0 and 5.0 wt% (at all temperatures), w/o emulsions at 0.5 wt% (at 298 K) and 50.0 wt% (at all temperatures), and diluted bitumen at 90.0 wt%. As expected, o/w emulsions were less viscous than w/o emulsions, reconfirming the

identified emulsion types. The viscosities of these o/w emulsions range between 40 cp and 60 cp at 1.0 sec^{-1} , and between 4 cp and 10 cp at 10.0 sec^{-1} at 298 K. At 323 K, they range between 90 cp and 138 cp at 1.0 sec^{-1} and between 13 cp and 33 cp at 10.0 sec^{-1} . At 353 K, viscosities of o/w emulsion are between 62 cp and 130 cp at 1.0 sec^{-1} and 16 cp and 42 cp at 10.0 sec^{-1} . At a given TETA concentrations, the viscosity of o/w emulsion does not correlate clearly with temperature. This is because the bitumen content in o/w emulsion increases as temperature increases (Table 1).

Using the same rheometer (section 2.4), the viscosity of the original bitumen was measured to be 9040 cp at 323 K and 690 cp at 353 K. Newtonian behavior was confirmed for this bitumen sample. The bitumen viscosity was not measured at 298 K because of the torque limit of the rheometer. The viscosity correlation given by Baek et al. (2017) for this bitumen sample calculates 447,000 cp at 298 K and atmospheric pressure. In comparison to these viscosities of the original bitumen, o/w emulsions are 4–5 orders of magnitude less viscous at 298 K, 2 to 3 orders of magnitude less viscous at 323 K, and 1 to 2 orders of magnitude less viscous at 353 K.

4. Conclusions

The main objective of this research was to present the ability of an organic alkali to create o/w emulsions that are much more mobile than the original bitumen. Because of the lack of experimental data for bitumen emulsification with organic alkali in the literature, this paper presented fundamental experimental data of phase behavior and viscosity for emulsions created for mixtures of Athabasca-bitumen, TETA, and NaCl brine.

The phase behavior study was based on 108 samples for different alkali concentrations, salinities, and WORs at temperatures from 293 K to 373 K. Viscosities and bitumen contents of o/w emulsions were

Table 2

(Section 3-2). Emulsion viscosities for samples at the salinity of 1000 ppm and water-oil-ratio (WOR) of 7:3, after aging for 3 weeks.

a. Temperature = 298 K					
TETA Concentration [wt%]	0.5	2.0	5.0	50.0	90.0
Shear Rate [1/s]	Viscosity [cp]	Viscosity [cp]	Viscosity [cp]	Viscosity [cp]	Viscosity [cp]
0.10	155360.0	447.3	210.4	100360.0	1577.9
0.18	153030.0	302.3	115.4	102540.0	1482.7
0.32	146430.0	186.9	74.3	103500.0	1231.5
0.56	133340.0	87.2	57.7	104700.0	800.9
1.00	120010.0	59.8	39.6	105050.0	454.5
1.78	107110.0	37.1	26.1	100410.0	314.2
3.16	93112.3	19.9	12.5	91256.3	170.6
5.62	83634.3	12.4	6.4	82145.4	124.8
10.00	74869.9	9.6	4.4	78709.1	112.8
17.78	63073.3	6.1	3.8	69098.2	103.9
31.62	49191.5	4.1	2.7	58675.6	93.4
56.23	34652.3	3.3	2.5	45412.5	89.9
100.0	26195.7	4.7	2.4	- (*)	90.0
b. Temperature = 323 K					
TETA Concentration [wt%]	0.5	2.0	5.0	50.0	90.0
Shear Rate [1/s]	Viscosity [cp]	Viscosity [cp]	Viscosity [cp]	Viscosity [cp]	Viscosity [cp]
0.10	363.9	405.3	440.4	5741.9	629.1
0.18	287.5	240.6	379.6	5832.2	577.6
0.32	209.2	200.4	274.8	5891.7	519.9
0.56	136.1	164.4	192.4	5936.3	449.7
1.00	90.3	138.0	135.5	5867.7	381.8
1.78	55.6	110.0	98.6	5768.8	323.2
3.16	34.8	78.9	79.9	5578.6	255.4
5.62	17.6	40.9	41.5	5296.5	264.3
10.00	13.0	15.8	32.9	5166.0	184.0
17.78	9.0	7.4	18.2	4862.9	122.6
31.62	5.2	4.5	8.7	4779.5	109.6
56.23	4.2	2.8	6.2	4991.3	66.0
100.0	3.8	2.3	4.4	4943.8	49.1
c. Temperature = 353 K					
TETA Concentration [wt%]	0.5	2.0	5.0	50.0	90.0
Shear Rate [1/s]	Viscosity [cp]	Viscosity [cp]	Viscosity [cp]	Viscosity [cp]	Viscosity [cp]
0.10	354.6	178.6	194.2	927.4	333.9
0.18	239.3	114.8	144.5	873.8	272.1
0.32	196.0	84.9	110.3	841.3	219.2
0.56	218.9	69.4	84.2	823.7	189.1
1.00	130.4	61.5	64.1	800.8	153.2
1.78	96.6	46.2	47.5	791.3	122.7
3.16	80.3	34.2	34.3	773.9	99.2
5.62	57.9	26.9	22.1	760.7	79.1
10.00	41.7	18.9	15.6	758.3	65.7
17.78	29.4	16.4	10.2	758.2	53.2
31.62	21.3	12.2	7.2	756.3	43.5
56.23	13.9	9.1	4.7	778.0	33.7
100.0	7.8	6.7	3.9	777.1	27.0

(*) measurement failed due to the maximum torque limit of the rheometer.

measured for selected emulsion samples at a WOR of 7:3 and a brine salinity of 1000 ppm at temperatures from 293 K to 353 K.

It was confirmed that o/w emulsions can be created with a small amount of organic alkali. In addition, the o/w emulsions were considerably less viscous than the original bitumen. That is, the o/w emulsions can be an effective bitumen carrier to enhance in-situ bitumen flow in SAGD. More specific findings are as follows:

- It was possible to create o/w emulsions by adding a small amount of TETA to Athabasca bitumen and NaCl brine. Results showed that o/w emulsions tend to occur at low TETA concentrations (< 10.0 wt %) and low salinities (< 1000 ppm). As TETA concentration increase, w/o emulsions appeared. A diluted bitumen was observed to

be a single phase at the highest TETA concentration studied, 90.0 wt %.

- Single-phase o/w emulsification, which is desirable as a bitumen carrier, was observed for TETA concentrations below 5.0 wt% at salinities 0 ppm and 1000 ppm at 373 K. An oil-continuous phase tended to appear in the presence of o/w emulsion with decreasing temperature, or with increasing alkali concentration, or increasing salinity.
- How much bitumen is contained in o/w emulsion is an important indicator of the effectiveness of o/w emulsion as a bitumen carrier. Therefore, bitumen contents in emulsions were measured for emulsion samples at a WOR of 7:3 for TETA concentrations below 5.0 wt% at temperatures between 298 K and 353 K. Results show

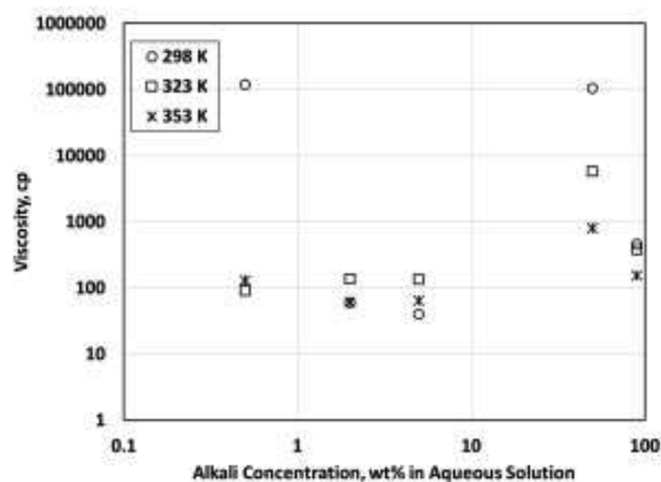
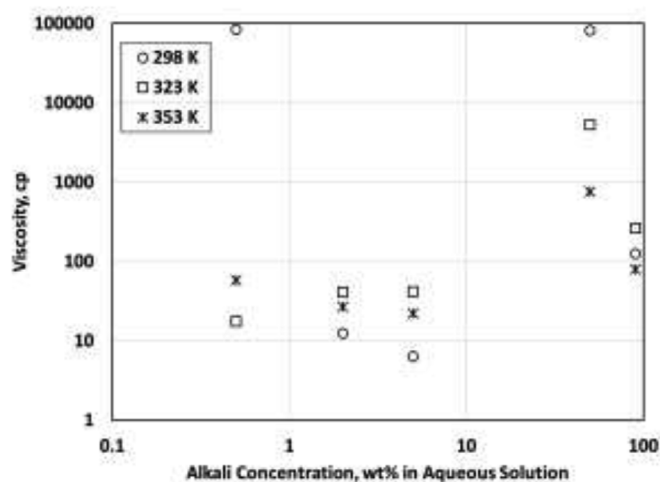
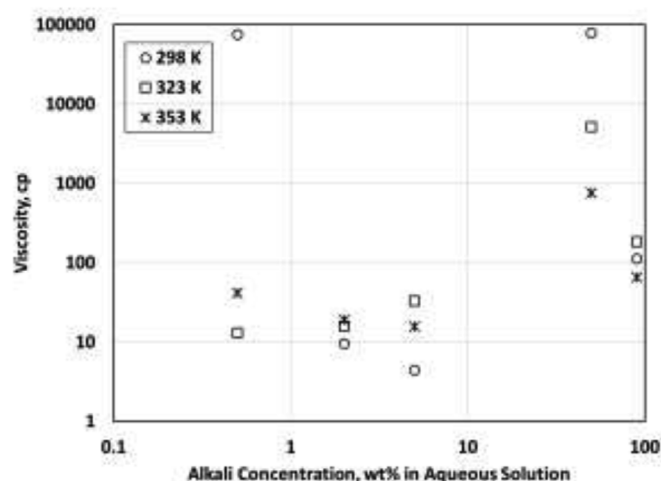
a. Shear rate of 1.0 sec⁻¹b. Shear rate of 5.6 sec⁻¹c. Shear rate of 10 sec⁻¹

Fig. 7. (Section 3-2). Viscosities of emulsions for samples at the salinity of 1000 ppm and WOR of 7:3 after aging for 3 weeks at three different shear rates; a. 1.0 sec⁻¹, b. 5.6 sec⁻¹, and c. 10.0 sec⁻¹. There are three types of fluids in this figure: o/w emulsions at TETA concentrations of 2.0 wt% and 5.0 wt% at all temperatures and 0.5 wt% at 323 K and 353 K w/o emulsions for 0.5 wt% at 298 K and 50.0 wt% at all temperatures. And diluted bitumen at 90.0 wt%.

that the bitumen content in o/w emulsion was the highest for 2.0 wt % TETA samples at the three temperatures. The bitumen content in o/w emulsion increased with increasing temperature (Table 1).

- A significant viscosity reduction was observed by o/w emulsification in comparison with the original bitumen. Viscosities were measured for selected emulsion samples, all of which showed shear-thinning behavior. For example, the viscosities of o/w emulsions were between 40 cp and 60 cp at 1.0 sec⁻¹, and between 4 cp and 10 cp at 10.0 s⁻¹ at 298 K. At 323 K, they ranged between 90 cp and 138 cp at 1.0 sec⁻¹ and between 13 cp and 33 cp at 10.0 sec⁻¹. At 353 K, they were between 62 cp and 130 cp at 1.0 sec⁻¹ and 16 cp and 42 cp at 10.0 sec⁻¹. These results show that, in comparison with the original bitumen, o/w emulsions were 4–5 orders of magnitude less viscous at 298 K, 2 to 3 orders of magnitude less viscous at 323 K, and 1 to 2 orders of magnitude less viscous at 353 K.

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