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Oil-in-water emulsification of Athabasca bitumen with pyrrolidine solution

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ABSTRACT

This paper presents an experimental study of use of pyrrolidine solutions to induce the oil-in-water (o/w) emulsion of Athabasca bitumen without using synthetic surfactants. Pyrrolidine, an organic alkali, acts not only as an alkali that generates natural surfactants from acidic oil components in bitumen, but also as a cosolvent that improves the fluidity of the o/w emulsions.

Experimental results show that the o/w emulsions created by pyrrolidine solutions can result in a large mobility increase of bitumen because of their low viscosity and high bitumen content. O/w emulsions were observed at low pyrrolidine concentrations (below 20 wt% and as low as 0.5 wt%) and low salinities (0 and 1000 ppm). For example, the sample of 0.5 wt% pyrrolidine in 1000-ppm NaCl brine with 7:3 water-oil-ratio showed a single-phase o/w emulsion at all experimental temperatures from 298 K to 373 K. In comparison to the original bitumen, the o/w emulsion was 4–6 orders of magnitude less viscous at 298 K, 2–3 orders of magnitude less viscous at 323 K, and 1–2 orders of magnitude less viscous at 353 K.

The affinity of the organic alkali for asphaltic bitumen is important for o/w emulsification at a wide range of temperatures. Pyrrolidine is superior to the other organic alkalis tested, diethylamine and triethylenetetramine, likely because the cyclic structure makes pyrrolidine more compatible with the asphaltic bitumen. The favorable result with pyrrolidine is also confirmed by the Hansen solubility dispersion parameter.

1. Introduction

Bitumen is highly viscous because of its asphaltene content (e.g., 20 wt% n-pentane insoluble), and it is often immobile at reservoir conditions. Steam injection is widely used to recover bitumen, in which the latent heat injected can effectively mobilize the bitumen near thermal fronts. However, steam injection methods, such as cyclic steam stimulation (CSS) and steam assisted gravity drainage (SAGD), are energy-intensive, and their efficiency is highly sensitive to reservoir properties, such as heterogeneous permeability, porosity, thickness, and phase saturations [1].

To improve the efficiency of these steam injection methods, solvent-steam co-injection has been tested at lab and field scales [2–9]. Solvent-steam co-injection aims to recover bitumen more efficiently by using the heating and dilution mechanisms together. These studies focused mainly on hydrocarbon solvents, such as propane, butane, and diluent, which is a mixture of pentane and heavier hydrocarbons [4,5,7–10]. Dimethyl ether (DME) was recently investigated as a potential additive to steam [11–13]. Unlike hydrocarbon solvents, it is soluble in both oil and water. It was shown that the solubility of DME in oil and water can yield unique mechanisms of bitumen recovery through reducing steam-oil ratio (SOR) and increasing solvent recovery [13].

If it is properly implemented, solvent-steam co-injection yields a reduction of SOR in comparison to the conventional steam injection methods. However, the presence of condensed water near the thermal fronts adversely affects the oil mobility along the edge of a steam chamber [14,15]. The current research is motivated by the fact that the water throughput is inherently large in steam injection. It is expected that bitumen can be efficiently transported in the form of o/w emulsion if the emulsion is rich in bitumen and much less viscous than the original bitumen.

Indeed, researchers have studied the emulsification of heavy oil by different methods for different purposes. Alkali injection for heavy oil recovery has been studied in water flooding processes, such as alkaline-surfactant, alkaline-surfactant-polymer, and alkaline-cosolvent-polymer flooding [16–27]. Alkalis in these processes are necessary to form natural surfactants by reaction with acidic oil components. Different combinations of alkalis, salts, surfactants, co-solvents, and polymers were tested to achieve ultra-low interfacial tension in these studies. For pipeline transportation of heavy oil, o/w emulsion viscosity was studied with different surfactants, alkalis, and solvents at different water-oil-ratios (WORs) and shear rates [28–33].

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Nomenclature

cp	centipoise
CSS	cyclic steam stimulation
DEA	diethylamine
DME	dimethyl ether
K	kelvin
KOH	potassium hydroxide
MW	molecular weight, g/mol
NaCl	sodium chloride
Na_2CO_3	sodium carbonate
o/w	oil-in-water
ppm	parts per million
SAGD	steam assisted gravity drainage
SARA	saturates, aromatics, resins, asphaltenes
SOR	steam-oil-ratio
TETA	triethylenetetramine
vol.%	volume %
w/o	water-in-oil
WOR	water-oil-ratio
wt%	weight %

Synthetic surfactants were also studied as steam additives for SAGD and CSS [34–36]. They used commercially available hydrophilic viscosity reducers [34], hydrophilic surfactants [36], and thin film spreading agents [35] to form o/w emulsions or to demulsify water-in-oil (w/o) emulsion to enhance in-situ 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.

As for use of alkalis with no synthetic surfactants, sodium carbonate has been studied for bitumen emulsification by natural surfactants [30,37]. It was used to activate natural surfactants and created o/w emulsions from Iranian heavy crude oil [30] and Cerro Negro bitumen [37]. In both studies, o/w emulsions were observed at the sodium carbonate concentration range from 2000 to 10,000 ppm. However, sodium carbonate cannot be transported as part of the vapor in steam-injection processes, such as SAGD. Kim et al. [38] studied alkali-steam co-injection for SAGD. They injected steam with an alkali into a micromodel chip, and observed significantly increased oil recovery by creating o/w emulsions. However, the alkali used was not specified in their paper.

Unlike other studies of heavy oil emulsification, this research is concentrated on bitumen-in-water emulsification by using an organic alkali without using additional surfactants or cosolvents. Organic alkali can act as alkali and cosolvent, and use of a single component with multiple functions can yield a simpler solution to enhancement of bitumen transport. To this end, it is important to find an optimal type of organic alkalis that can form the o/w emulsion that is much less viscous than the original bitumen, yet has a high concentration of bitumen.

Bitumen is a complex mixture of hydrocarbons and typically contains asphaltenes and resins at high concentrations. It has been found that asphaltenes and resins in bitumen interact with water and play the critical role to create stable emulsions [39–45]. In addition, the ratio between asphaltenes and resins is also the important factor to create emulsions [46–48].

There are only a limited amount of data for bitumen emulsification with organic alkalis. It is of fundamental importance to study the phase behavior and rheology of emulsions created by bitumen and organic alkali solution, prior to validation by a coreflooding experiment or a field test. Baek et al. [49,50] studied two different organic alkalis, diethylamine (DEA) and triethylenetetramine (TETA), for bitumen emulsification. They showed that aqueous solutions of these organic alkalis created single-phase o/w emulsions of low viscosity with Athabasca bitumen. Based on the studies of Baek et al., we speculated that the chemical structure of the organic alkali should influence the resulting emulsion phase behavior and rheology as it is acting as cosolvent in these mixtures.

Therefore, the current research is to investigate an organic alkali which contains a cyclic structure unlike DEA and TETA. Pyrrolidine was chosen among cyclic amines because its volatility (vapor pressure) is similar to n-C_6 and n-C_7, which have been studied as suitable hydrocarbon solvents for SAGD in Athabasca bitumen reservoirs [5].

This paper addresses the following questions:

(1) Investigate whether o/w emulsions can be formed by adding pyrrolidine to Athabasca bitumen and NaCl brine
(2) Establish phase behavior data for bitumen emulsification at different pyrrolidine concentrations, WORs, brine salinities, and temperatures
(3) Measure the oil content and viscosity of o/w emulsion to evaluate the effectiveness of the o/w emulsion as a bitumen carrier
(4) Compare three organic alkalis, DEA, TETA, and pyrrolidine, in terms of bitumen emulsification.

Section 2 presents the materials and experimental procedure of this research. Results of phase behavior and viscosity measurements are presented in Section 3. The results are discussed in Section 4 in terms of the effect of the chemical structure of the organic alkali on o/w emulsification of bitumen. Finally, key conclusions are summarized in Section 5.

2. Materials and experimental procedure

2.1. Materials

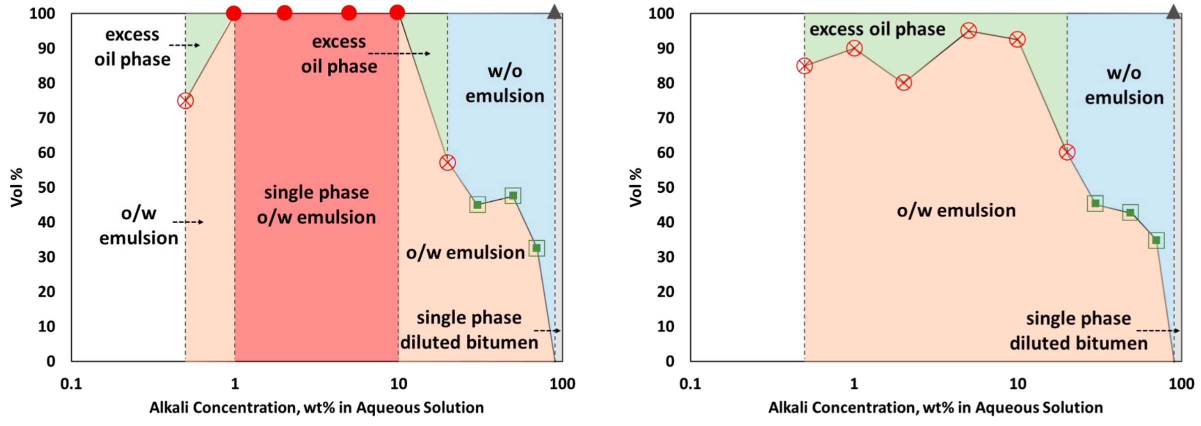
2.1.1. Bitumen

Dehydrated Athabasca bitumen was used in this research. The molecular weight (MW) of the bitumen sample is 532 g/mol. The density is 0.985 g/ml at 335 K and atmospheric pressure. The SARA composition is 24.5 wt% saturates, 36.6 wt% aromatics, 21.1 wt% resins, and 17.8 wt% asphaltenes (pentane insoluble). Detailed data of viscosity and density for this bitumen sample can be found in Baek et al. [11].

The total acid number (TAN) is 3.56 mg-KOH/g-oil based on the method of Fan and Buckley [51]. The acid number of oil is an important factor for alkali-based oil recovery methods. For example, Cooke et al. [52] stated that the required acid number for an alkali-based oil recovery method was 1.5 mg-KOH/g-oil. Ge et al. [53] showed sandpack flooding experiments with four oil samples with acid numbers between 1.85 and 4.66 mg-KOH/g-oil. A higher oil recovery was obtained when the oil had a higher acid number in their experiments. The acid number of the bitumen sample in this research, 3.56 mg-KOH/g-oil, indicates that the bitumen contains a sufficient amount of acidic components to create natural surfactants by reaction with an organic alkali.

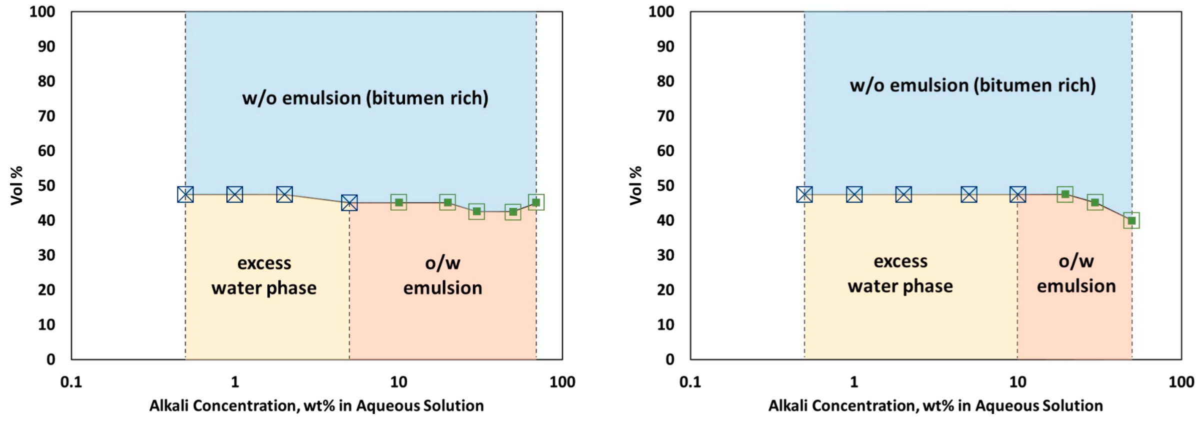
Table 1
pH of pyrrolidine solutions at room temperature.

Pyrrolidine concentration [wt%]	0.5	1	2	5	10	20	30	50	70	90
pH	10.6	11.4	11.4	11.5	11.6	11.6	11.7	11.6	11.5	10.7



a. WOR 5:5, Salinity: 0 ppm

b. WOR 5:5, Salinity: 1,000 ppm



c. WOR 5:5, Salinity: 30,000 ppm

d. WOR 5:5, Salinity: 100,000 ppm

Fig. 1. Emulsion phase behavior at 5:5 water-oil-ratio (WOR) at 373 K: a. 0 ppm, b. 1000 ppm, c. 30,000 ppm, and d. 100,000 ppm. Single-phase o/w emulsions were observed at 0 ppm. At low salinities (0 and 1000 ppm), o/w emulsions with excess oil phase were dominant below 20 wt% pyrrolidine concentration. At higher salinities (30,000 and 100,000 ppm), bitumen-rich w/o emulsions were dominant over o/w emulsions. ●: 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.

2.1.2. *Organic alkali*

O/w emulsification of bitumen by using dimethylamine (DEA: $C_4H_{11}N$) and triethylenetetramine (TETA: $C_6H_{18}N_4$) were studied in our previous research [49,50]. In this research, pyrrolidine (C_4H_9N) was studied for o/w emulsification of the same bitumen sample as the sample used in [49,50]. DEA, TETA, and pyrrolidine are organic alkalis with different chemical structures. Unlike DEA and TETA, pyrrolidine contains a cyclic structure, which is the main reason for the selection of pyrrolidine for this research. Pyrrolidine's MW and normal boiling temperature are 71 g/mol and 360 K, respectively. The pyrrolidine provided by Sigma-Aldrich has a purity higher than 99.5%.

A high pH of aqueous solution is usually required to create natural surfactants by the reaction of alkalis with acidic components in bitumen [54]. As shown in Table 1, it was confirmed that pyrrolidine can create a high pH aqueous phase when it dissolves into the aqueous phase. For example, the pH of aqueous solution with pyrrolidine ranged between 10.6 and 11.7 when it was mixed with 1000 ppm NaCl brine.

2.1.3. *Brine*

Analysis of the produced water from the production wells, from which the bitumen sample was taken, showed that the produced water only contained a few hundreds of ppm of NaCl [55,56]. Therefore, NaCl was used as the only salt in the brines tested in this research. Although the actual salinity is low in the produced water, different NaCl concentrations were prepared with deionized water for this research, ranging from 0 to 100,000 ppm.

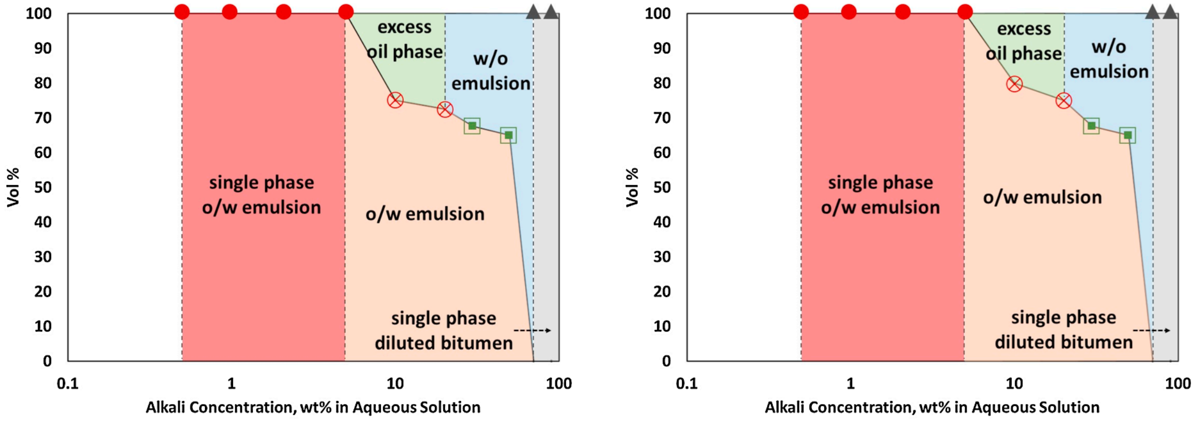
2.2. *Experimental procedure*

2.2.1. *Emulsion phase behavior*

Samples were prepared at 10 different pyrrolidine concentrations (0.5, 1, 2, 5, 10, 20, 30, 50, 70, and 90 wt% in aqueous phase) with 4 different salinities (0, 1000, 30,000, and 100,000 ppm) for 3 different WORs (5:5, 7:3, and 9:1). Because of NaCl's solubility limit in water, the maximum salinity tested is 30,000 ppm for 90 wt% pyrrolidine, and 100,000 ppm for 70 wt% pyrrolidine. As a result, emulsion phase behavior was studied for 111 samples at 373 K.

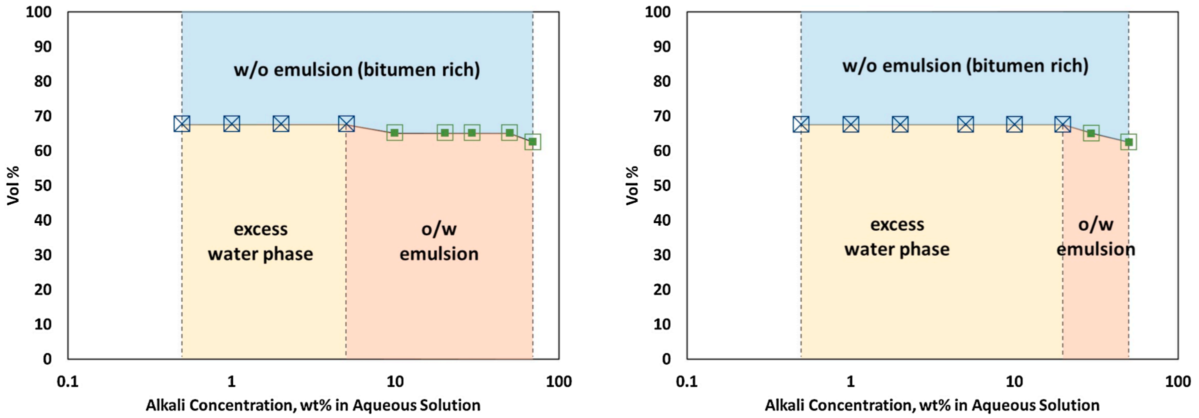
For each test, 4 ml sample was prepared in a 10 ml Pyrex pipette as explained below. First, the tip of a pipette was sealed by flame. Then, the aqueous phase was added in the pipette with specified amounts of brine and pyrrolidine. A WOR was set by adding heated bitumen (at 353 K) to the aqueous phase in the pipette. Once all components were added, argon gas was injected into the pipette as blanket gas. Finally, the neck of the pipette was sealed by flame. The samples were aged in an oven at 373 K for 3 weeks. During the aging period, all samples were mixed 4 times a day. Then, the samples were rested for 2 days before emulsion phase behavior was recorded at 373 K.

The pH values measured for the aqueous phase after mixing



a. WOR 7:3, Salinity: 0 ppm

b. WOR 7:3, Salinity: 1,000 ppm



c. WOR 7:3, Salinity: 30,000 ppm

d. WOR 7:3, Salinity: 100,000 ppm

Fig. 2. Emulsion phase behavior at 7:3 water-oil-ratio (WOR) at 373 K: a. 0 ppm, b. 1000 ppm, c. 30,000 ppm, and d. 100,000 ppm. At low salinities (0 and 1000 ppm), single-phase o/w emulsions were observed from 0.5 to 5 wt% pyrrolidine concentration. O/w emulsions with excess oil phase were dominant below 20 wt% pyrrolidine concentration. At higher salinities (30,000 and 100,000 ppm), bitumen-rich w/o emulsions were dominant over o/w emulsions. ●: 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.

indicated that all acidic components in bitumen had reacted with pyrrolidine. The minimum pH value was measured to be 9.8 for the sample of 0.5 wt% pyrrolidine with WOR 5:5.

Emulsion types (water-external and oil-external) were identified with several different methods: visual observation, emulsion volume, emulsion fluidity in a pipette, and the method used in Kumar et al. [21]. Kumar et al. determined 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. The opposite behavior was observed for w/o emulsions.

2.2.2. *Viscosity and bitumen content in emulsion*

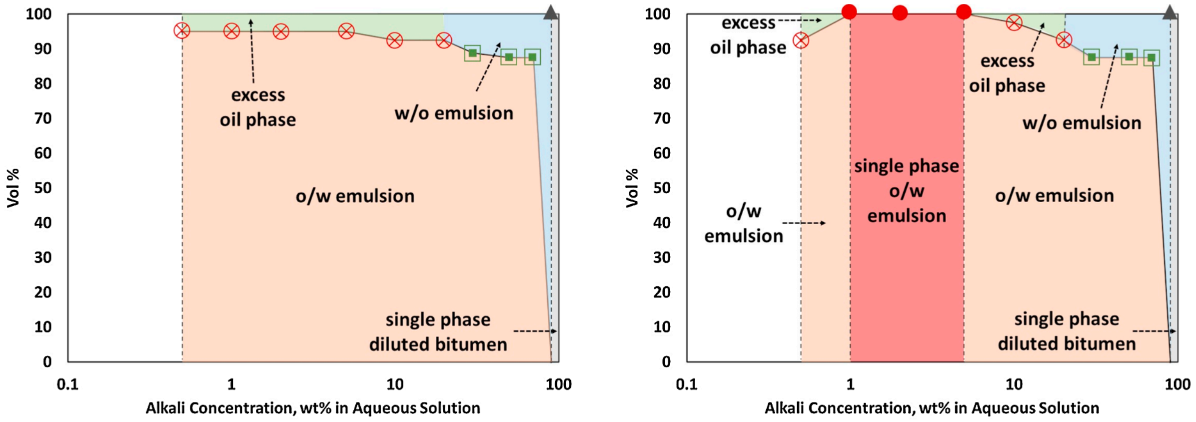
After the general emulsion phase behavior scans (Section 2.2.1), the viscosity and bitumen content in emulsions were measured for selected samples: 5 pyrrolidine concentrations (0.5, 2, 5, 50, and 90 wt% in aqueous phase) at 1000 ppm and WOR 7:3. The salinity and WOR were selected by considering typical operating conditions in the oil field from which the bitumen sample was taken for this research.

For this more detailed analysis of specific emulsion samples, 8 ml of the sample was prepared in a 10 ml Pyrex pipette using the same preparation procedure of emulsion phase behavior. Phase behavior of these samples was 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).

The viscosity of emulsion phase was measured by a rheometer (Model: ARES LS-1 from TA Instruments) with 50 mm diameter parallel bottom and upper plates at 3 different temperatures (298 K, 323 K, and 353 K). Viscosity measurement temperature was limited by pyrrolidine's normal boiling temperature (360 K). For each viscosity measurement, an emulsion sample taken from a pipette was transferred on the bottom parallel plate of the rheometer. Different gap sizes were applied 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}. The lower limit of torque during viscosity measurement was set to 0.74 μNm because measurements at lower torques might be unreliable. For each emulsion sample, an average viscosity was reported based on 2–4 times of repeated measurements.

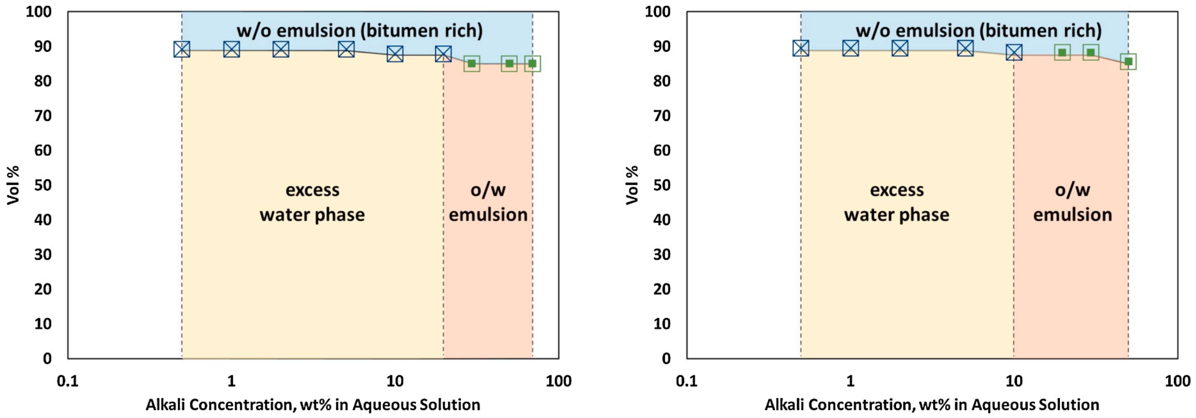
Special care was taken as described in Tagavifar et al. [57] to avoid any possible errors in the viscosity measurement using this particular rheometer. For each measurement, a new sample was used to prevent any alteration of emulsion rheology through experiencing high shear rates. Although it is ideal to measure viscosity right after the loading of a sample, samples were placed on the rheometer for several minutes for viscosity measurements at 323 K and 353 K to reach the target temperature.

The amount of bitumen in o/w emulsions was measured by separating bitumen 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



a. WOR 9:1, Salinity: 0 ppm

b. WOR 9:1, Salinity: 1,000 ppm



c. WOR 9:1, Salinity: 30,000 ppm

d. WOR 9:1, Salinity: 100,000 ppm

Fig. 3. Emulsion phase behavior at 9:1 water-oil-ratio (WOR) at 373 K: a. 0 ppm, b. 1000 ppm, c. 30,000 ppm, and d. 100,000 ppm. Single-phase o/w emulsions were observed at 1000 ppm. At low salinities (0 and 1000 ppm), o/w emulsions with excess oil phase were dominant below 20 wt% pyrrolidine concentration. At higher salinities (30,000 and 100,000 ppm), bitumen-rich w/o emulsions were dominant over o/w emulsions. ●: 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.

total solution of 3 ml. This mixture of emulsion and HCl was stirred until transparent water was separated from bitumen along with the protonated alkali. Then, the volume of bitumen was obtained by measuring the volume of separated water. The material balance for the entire sample (2.4 ml of bitumen in the total sample of 8 ml) was confirmed for the determination of the bitumen amount in o/w emulsions. For w/o emulsions, the bitumen content in emulsion was not measured since bitumen was existing only in the emulsion phase.

3. Results

3.1. Emulsion phase behavior

Results of the emulsion phase behavior for 111 samples at 373 K are summarized in Figs. 1–3. In these figures, phase types were identified based on the method described in Section 2.2.1. The observed phase behavior can be categorized into 5 types: 2 types for a single-phase and 3 types for two phases. The single-phase types are “o/w emulsion” and “diluted bitumen”. The two-phase types are “o/w emulsion with an excess-oil phase”, “w/o emulsion with an excess-water phase”, and “bitumen-rich w/o emulsion with water-rich o/w emulsion”. Table 2 presents the transition of bitumen-rich phase between o/w and w/o to clarify favorable conditions for o/w emulsification. It shows that o/w emulsion is dominant at low salinities (0 ppm and 1000 ppm) and low alkali concentrations (below 20 wt%). As an example, photos of emulsion samples with WOR 7:3 at 0 and 1000 ppm are presented in Fig. 4. Fig. 5 shows the phase behavior of samples with 1000 ppm NaCl and WOR 7:3 at 298 K, 323 K, and 353 K. These figures can be compared with Figs. 2b and 4b (at 373 K).

Observations based on these figures are explained below. First, o/w emulsion was dominant at low salinity (0 and 1000 ppm) and w/o emulsion was dominant at high salinity (30,000 and 100,000 ppm). The inversion of o/w to w/o emulsions with increasing salinity was also observed in many research publications [20,25,52,58–61]. With increasing salinity, the interaction between water molecules and salt ions increases compared to that between water molecules and surfactants. As a result, the interfacial tension (IFT) between emulsion and oil decreases whereas the IFT between emulsion and water increases with increasing salinity, as experimentally shown by Bera et al. [60] and Healy et al. [61]. Acevedo et al. [37] observed in their experiment that the IFT between oil and aqueous solution increased with increasing NaCl concentration, resulting in the disappearance of the ultra-low IFT region that existed at lower NaCl concentrations.

Second, o/w emulsions were dominant at low pyrrolidine concentrations, and w/o emulsion appeared with increasing pyrrolidine concentration. At the pyrrolidine concentration of 90 wt%, single-phase bitumen was highly mobile, indicating a solvent-diluted bitumen phase. Winsor [62] presented that the addition of water-soluble organic liquid

Table 2

Bitumen-rich emulsion types with respect to alkali concentration, WOR, and salinity based on 111 samples at 373 K. This table clearly shows that o/w emulsion is dominant at low salinities (0 and 1000 ppm) and low alkali concentrations (lower than 20 wt%).

o/w	oil-in-water emulsion
w/o	water-in-oil emulsion
dilution	diluted bitumen (not emulsion)

Salinity WOR	0 ppm Pyrrolidine Concentration [wt%]									
	0.5	1	2	5	10	20	30	50	70	90
5:5	o/w	o/w	o/w	o/w	o/w	o/w	w/o	w/o	w/o	dilution
7:3	o/w	o/w	o/w	o/w	o/w	o/w	w/o	w/o	dilution	dilution
9:1	o/w	o/w	o/w	o/w	o/w	o/w	w/o	w/o	w/o	dilution

Salinity WOR	1000 ppm Pyrrolidine Concentration [wt%]									
	0.5	1	2	5	10	20	30	50	70	90
5:5	o/w	o/w	o/w	o/w	o/w	o/w	w/o	w/o	w/o	dilution
7:3	o/w	o/w	o/w	o/w	o/w	o/w	w/o	w/o	dilution	dilution
9:1	o/w	o/w	o/w	o/w	o/w	o/w	w/o	w/o	w/o	dilution

Salinity WOR	30,000 ppm Pyrrolidine Concentration [wt%]								
	0.5	1	2	5	10	20	30	50	70
5:5	w/o	w/o	w/o	w/o	w/o	w/o	w/o	w/o	w/o
7:3	w/o	w/o	w/o	w/o	w/o	w/o	w/o	w/o	w/o
9:1	w/o	w/o	w/o	w/o	w/o	w/o	w/o	w/o	w/o

Salinity WOR	100,000 ppm Pyrrolidine Concentration [wt%]							
	0.5	1	2	5	10	20	30	50
5:5	w/o	w/o	w/o	w/o	w/o	w/o	w/o	w/o
7:3	w/o	w/o	w/o	w/o	w/o	w/o	w/o	w/o
9:1	w/o	w/o	w/o	w/o	w/o	w/o	w/o	w/o

can invert o/w to w/o emulsion. Indeed, the inversion from o/w to w/o emulsion was observed with increasing pyrrolidine concentration. This kind of emulsion inversion was also found by Salager et al. [63], in which o/w emulsions were inverted to w/o emulsions with increasing pentanol concentration at a fixed salinity and WOR. The pH values of o/w emulsion samples with 0.5, 2, and 5 wt% pyrrolidine at WOR 7:3 were greater than 10 at room temperature (Fig. 5). This indicates that acidic components were reacted with pyrrolidine and therefore, the amounts of natural surfactants were similar for the o/w emulsion samples. That is, it is conceivable that the effect of pyrrolidine on emulsion phase behavior came from the excess amount of pyrrolidine as cosolvent, rather than the concentration of natural surfactants. Results in Fig. 5 indicate that 0.5 wt% pyrrolidine was an optimal concentration in comparison to 2 wt% and 5 wt%, and that the excess amount of pyrrolidine worked as cosolvent more effectively at 5 wt% than at 2 wt %. The latter observation may come from the dilution of bitumen that was more significant for the 5- wt% pyrrolidine sample.

Third, with increasing WOR, o/w emulsions became lean in bitumen owing to a smaller amount of natural surfactants. Inversion from o/w to w/o emulsion with increasing WOR was studied in other studies [20,25,59]. The effect of WOR on emulsion phase behavior depends on properties of oil and therefore, the type of natural surfactants activated by alkalis. For example, Fortenberry et al. [20] studied the effect of WOR on emulsion phase behavior with different cosolvents, where o/w emulsions became more dominant with increasing WOR.

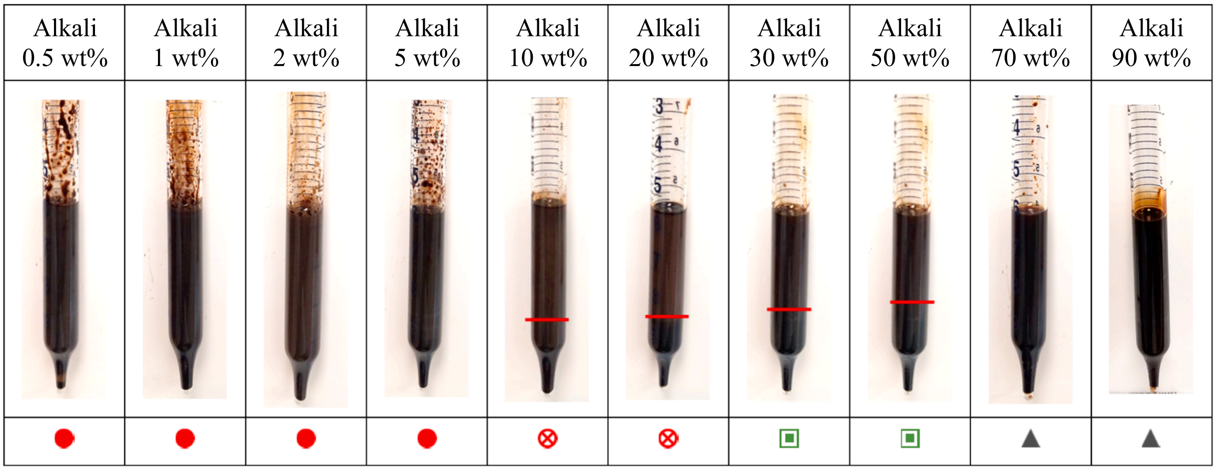
Fig. 5 shows that higher temperature was more favorable for creating a single-phase o/w emulsion. The effect of temperature on emulsion phase behavior may be explained through the temperature effect on the IFT between oil and aqueous solution. However, the uncertainty in natural surfactant properties makes it difficult to give a systematic explanation of the temperature effect on phase behavior in this research.

At a given surfactant concentration, the IFT can either decrease or increase with increasing temperature depending on the salinity [64,65]. At a given salinity, it was observed that IFT decreased up to a certain temperature and increased at higher temperatures [66]. The IFT reduction between bitumen and surfactant solution with increasing temperature was measured by Isaacs and Smolek [64]. In their experiment, the IFT between bitumen and surfactant solution was decreased from 323 to 373 K at the NaCl salinity range between 0 and 2500 ppm. Natural surfactants in this research may have given a similar trend, in which the natural surfactants at 1000-ppm NaCl brine decreased the IFT between bitumen and aqueous phase as temperature increased from 298 K to 373 K.

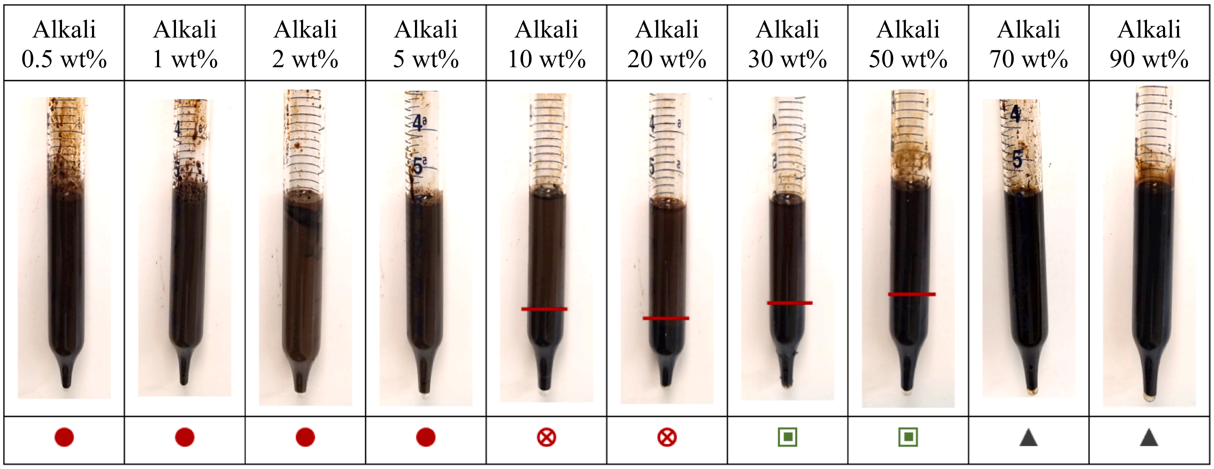
To recap on the main results in this section, an optimal range for o/w emulsification was found at small concentrations of pyrrolidine at salinities below 1000 ppm. In particular, the most desirable emulsification of bitumen in water as a single phase was observed at the following conditions: (1) for WOR 9:1, 1–5 wt% pyrrolidine at 1000 ppm, (2) for WOR 7:3, 0.5–5 wt% pyrrolidine at 0 and 1000 ppm, and (3) for WOR 5:5, 1–10 wt% pyrrolidine at 0 ppm.

3.2. Bitumen content and viscosity of emulsions

This section presents the results of bitumen contents in o/w emulsions and viscosities of emulsions for selected samples. The samples



a. WOR 7:3, Salinity: 0 ppm, Temperature 373 K



b. WOR 7:3, Salinity: 1000 ppm, Temperature 373 K

Fig. 4. Photos of emulsion phase behavior for different pyrrolidine concentrations with 7:3 water-oil-ratio (WOR) at 0 and 1000 ppm at 373 K. From 0.5 to 5 wt% of pyrrolidine, single-phase o/w emulsions were created. At 10 and 20 wt%, o/w emulsions with an excess oil phase were observed. At 30 and 50 wt%, w/o emulsions (bitumen-rich) with o/w emulsion (water-rich) were observed. Note that even a small amount of bitumen in the aqueous phase can make o/w emulsions very dark. Above 70 wt%, bitumen was diluted by pyrrolidine solution. ●: 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.

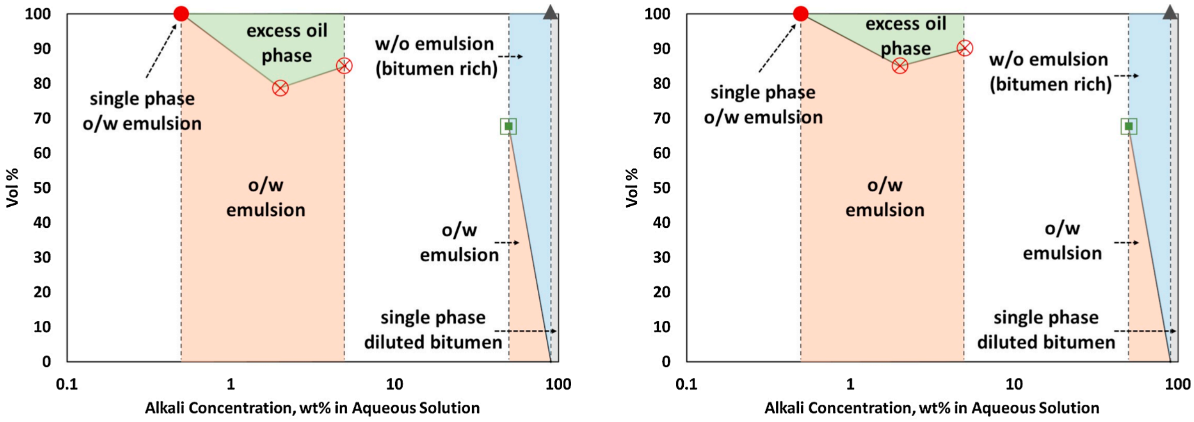
studies were 5 pyrrolidine concentrations (0.5, 2, 5, 50, and 90 wt%) at WOR of 7:3 and 1000 ppm salinity at 3 different temperatures (298 K, 323 K, and 353 K) as explained in Section 2.2.2. The phase behavior for these samples were previously given in Fig. 5.

Table 3 presents the bitumen contents in o/w emulsions at different temperatures. Measurement of the bitumen content in emulsion for samples with shorter periods of aging, 1 week and 2 weeks, showed that the bitumen content was steady after 1 week. Figs. 2b and 5 showed that a single-phase o/w emulsion was created with 0.5 wt% pyrrolidine sample for all temperatures. These emulsion samples have the maximum bitumen content, 2.4 ml, which is 30% of the entire emulsion volume.

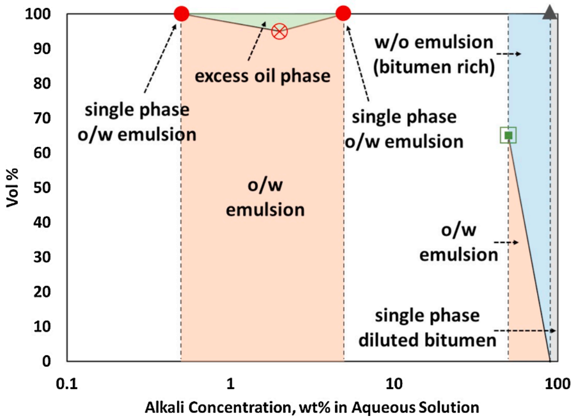
As shown in Fig. 5, the amount of the excess oil phase for these pyrrolidine concentrations of 2 wt% and 5 wt% decreases with increasing temperature. At 373 K, the excess oil phase was not observed as the bitumen was completely emulsified in water as shown in Figs. 2b and 4b.

Results of the viscosity measurement are presented in Table 4 and Fig. 6. Shear-thinning behavior was observed for all fluids studied, except for the original bitumen. The shear-thinning behavior indicates hydrodynamic interaction and deformation of dispersed droplets [67,68]. However, the w/o emulsion at 50 wt% pyrrolidine concentration was only weakly shear-thinning likely because there was only a small amount of dispersed water in this oil-external emulsion [69].

The bitumen content and temperature affect the viscosity of o/w emulsions in a complex manner. With increasing temperature, the bitumen content tends to increase in the o/w emulsion, but the viscosity of bitumen itself decreases. The effect of temperature on o/w emulsion viscosity can be observed for the case of 0.5 wt% pyrrolidine; i.e., the viscosities of the single-phase o/w emulsion with 0.5 wt% pyrrolidine at 298 K were similar to those at 323 K. At 353 K, however, the o/w emulsion became much less viscous especially at lower shear rates. The effect of an increased oil content in o/w emulsion can be observed for the viscosity data obtained for 2 wt% pyrrolidine samples at 298 K and 323 K, where the o/w emulsion viscosity increases with increasing temperature. The data for 5 wt% pyrrolidine samples at the three temperatures in Table 4 show that the viscosity of o/w emulsion decreased with increasing temperature in spite of the increased oil content at 353 K.



a. Temperature 298 K b. Temperature 323 K



c. Temperature 353 K

Fig. 5. Emulsion phase behavior at 278 K, 323 K and 353 K. Salinity and water-oil-ratio were fixed at 1000 ppm and WOR 7:3. 0.5 wt% pyrrolidine sample created a single-phase o/w emulsion at all temperatures. At pyrrolidine concentrations below 5 wt%, it clearly shows that the vol.% of o/w emulsions became larger with increasing temperature, indicating o/w emulsions turned into a single-phase o/w emulsion. At 373 K, these o/w emulsions became a single-phase as shown in Figs. 2b and 4b. ●: 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.

As expected, w/o emulsions created with 50 wt% pyrrolidine were more viscous than o/w emulsions created with lower pyrrolidine concentrations. The effect of temperature on viscosity reduction is more prominent for w/o emulsions as the external phase is oil. At the shear rate of 1 sec^{-1}, for example, the viscosity decreased from 15,750 cp at 298 K to 418 cp at 353 K. However, these w/o emulsions were substantially less viscous than the original bitumen at a given temperature, indicating the dilution of bitumen by pyrrolidine.

The viscosity of the bitumen measured by the same rheometer (Section 2.2.2) was 9040 cp at 323 K and 690 cp at 353 K. Newtonian behavior was confirmed for the bitumen sample as shown in Fig. 6. At 298 K, the bitumen viscosity was not measured by the rheometer because of the limitation in torque. However, Baek et al. [11] presented a viscosity correlation for this bitumen based on measurements using an in-line viscometer, which calculates 447,000 cp at 298 K. In comparison with the original bitumen, o/w emulsions created by different pyrrolidine concentrations are 4–6 orders of magnitude less viscous at 298 K, 2–3 orders of magnitude less viscous at 323 K, and 1–2 orders of magnitude less viscous at 353 K.

The viscosity and the amount of bitumen in o/w emulsions indicate that o/w emulsions could be an effective bitumen carrier that contains a large amount of bitumen with a significantly lower viscosity than the viscosity of the original bitumen. Only a small amount of pyrrolidine (0.5 wt%) was enough to create a single-phase o/w emulsion at a wide range of temperatures.

4. Discussion

As mentioned in Section 2.1.2, the current research of bitumen emulsification with pyrrolidine used the same bitumen as that in Baek et al. [49,50], where diethylamine (DEA) and triethylenetetramine (TETA) were used as organic alkalis. This section first compares the main results with the three organic alkalis (DEA, TETA, and pyrrolidine), and then discuss the effect of the chemical structure of organic alkalis on the bitumen emulsification. It is reasonable to assume that the natural surfactants (soaps) created from the same bitumen were similar in the current research and Baek et al. [49,50]. Therefore, the difference among the three sets of results with different organic alkalis is attributed largely to differences of the organic alkalis as the cosolvent in the bitumen/NaCl-brine/alkali mixture.

Properties of DEA, pyrrolidine, and TETA are summarized in Table 5. DEA and pyrrolidine are secondary amines and similar to each other in terms of MW and chemical formula. However, the important difference is that DEA has an aliphatic hydrocarbon chain, whereas pyrrolidine has a cyclic structure. TETA contains three two-carbon aliphatic segments and 4 nitrogens. Appendices A and B present the bitumen emulsification with DEA and TETA [49,50].

Results of Baek et al. [49] showed that TETA was effective in o/w

Table 3
The amount of bitumen in o/w emulsions at 1000 ppm and 7:3 WOR. The amount of bitumen is 2.4 ml in the total of 8 ml of each sample. Samples with 0.5 wt% pyrrolidine created a single-phase o/w emulsion at all temperatures. It is clear that, as temperature increases, bitumen content in emulsion also increases for a given o/w emulsion. Refer to Fig. 5 for the corresponding phase behavior.

a. Temperature 298 K

Pyrrolidine concentration [wt%]	Emulsion type	Emulsion volume	Volumetric composition of emulsion			
			Bitumen		Brine	
			[ml]	[%]	[ml]	[%]
0.5	o/w	8.0	2.4	30	5.6	70
2	o/w	6.3	0.7	11	5.6	89
5	o/w	6.8	1.2	18	5.6	82

b. Temperature 323 K

Pyrrolidine concentration [wt%]	Emulsion type	Emulsion volume	Volumetric composition of emulsion			
			Bitumen		Brine	
			[ml]	[%]	[ml]	[%]
0.5	o/w	8.0	2.4	30	5.6	70
2	o/w	6.8	1.2	18	5.6	82
5	o/w	7.2	1.6	22	5.6	78

c. Temperature 353 K

Pyrrolidine concentration [wt%]	Emulsion type	Emulsion volume	Volumetric composition of emulsion			
			Bitumen		Brine	
			[ml]	[%]	[ml]	[%]
0.5	o/w	8.0	2.4	30	5.6	70
2	o/w	7.6	2.0	26	5.6	74
5	o/w	8.0	2.4	30	5.6	70

emulsification of bitumen only at high temperatures. At WOR 7:3 and 1000 ppm, for example, TETA gave a single-phase o/w emulsion at 373 K (Fig. A.2). At temperatures below 373 K, however, an o/w emulsion with a small amount of bitumen was created along with an excess bitumen phase. With 4 nitrogen atoms in TETA, TETA is the most polar compound among the three organic alkalis, resulting in a large solubility in water. The high polarity tends to make TETA sensitive to temperature in terms of affinity for the bitumen in the presence of water [11]. It is likely that TETA's polarity is too high for o/w emulsification of the bitumen for a wide range of temperatures.

In comparison to DEA and TETA, pyrrolidine created the single-phase o/w emulsion behavior at a wider range of temperatures. Also, the o/w emulsions created with pyrrolidine showed superior fluidity and rapid coalescence behavior after mixing when an o/w emulsion coexisted with an excess oil phase (Fig. B.1-3). This type of qualitative observations in addition to emulsion color and texture is a widely used technique for identification of low interfacial tension emulsions [70].

Potential reasons for pyrrolidine to be superior to DEA and TETA as cosolvent may include the higher level of affinity for bitumen, which is often highly asphaltic. The steric effect of the organic alkali as cosolvent is an important factor that affects the shape of the cosolvent, which in turn affects the size of asphaltenes aggregation in the bitumen emulsification. Asphaltenes are a group of complex compounds with multi-benzene rings. According to Larichev et al. [71], planar molecules (e.g., cyclic hydrocarbons due to the steric effect on their shapes) can fit into the asphaltene structure and replace asphaltene molecules with relatively small hydrocarbons. For example, they observed that cyclohexanol disaggregates asphaltenes whereas 1-hexanol aggregates asphaltenes, although they are similar in terms of MW and chemical formula. The steric effect likely makes pyrrolidine more compatible with the asphaltic bitumen than DEA and TETA. Although pyrrolidine has a greater polarity than DEA according to Table 5, our research results showed that the steric effect on the molecular shape is more important than polarity as cosolvent to create o/w emulsions with the bitumen studied.

The Hansen solubility dispersion parameter can be a good indicator for the affinity for bitumen. Larichev et al. [71] observed the disaggregation of asphaltenes when the Hansen solubility dispersion parameter of the chemical increases from 14.5 to 20. The Hansen solubility dispersion parameter is 14.9 for DEA and 17.9 for pyrrolidine [72]. Larichev et al. [71] studied the relationship between the dispersion parameter and asphaltene aggregation, based on which the size of asphaltene aggregation with pyrrolidine could be about 12% smaller than that with DEA.

Comparison of different organic alkalis for the same bitumen indicates that it is important to consider the affinity of the organic alkali as cosolvent for bitumen for o/w emulsification. There are possible parameters that can be used for selection of organic alkalis for o/w emulsification of bitumen, such as molecular structure and the Hansen solubility parameter.

5. Conclusions

This paper presented the fundamental data of phase behavior and viscosity for emulsions created by mixtures of Athabasca bitumen, pyrrolidine, and NaCl brine. The emulsion phase behavior was summarized by 111 samples with different pyrrolidine concentrations, brine salinities, and WORs at 373 K. Viscosities and bitumen contents in

Table 4
Emulsion viscosity (WOR 7:3, Salinity 1000 ppm).

a. Temperature 298 K

Pyrrolidine concentration Emulsion type Shear rate [1/sec]	0.5 wt% o/w Viscosity [cp]	2 wt% o/w Viscosity [cp]	5 wt% o/w Viscosity [cp]	50 wt% w/o Viscosity [cp]	90 wt% dilution Viscosity [cp]
0.1	176.0	83.3	130.0	17801.3	102.2
0.2	168.0	65.5	103.5	17761.2	63.5
0.3	112.4	44.5	75.8	17535.3	42.7
0.6	69.9	30.0	55.6	16793.4	29.2
1.0	40.1	20.3	36.3	15750.8	22.2
1.8	25.7	13.0	22.7	14370.6	16.4
3.2	14.6	8.0	15.4	13659.8	13.4
5.6	11.1	4.9	10.2	13014.9	11.7
10.0	8.2	3.9	8.0	10400.0	11.2
17.8	6.7	2.8	6.4	8296.3	10.0
31.6	5.5	2.2	5.2	7167.6	9.4
56.2	4.9	1.8	4.6	5863.5	8.6
100.0	4.5	1.6	4.2	5115.7	9.2

b. Temperature 323 K

Pyrrolidine concentration Emulsion type Shear rate [1/sec]	0.5 wt% o/w Viscosity [cp]	2 wt% o/w Viscosity [cp]	5 wt% o/w Viscosity [cp]	50 wt% w/o Viscosity [cp]	90 wt% dilution Viscosity [cp]
0.1	235.1	176.7	132.6	([a])	54.5
0.2	177.2	167.3	105.8	2006.4	56.7
0.3	125.3	146.5	86.8	1993.8	61.1
0.6	81.9	134.3	72.4	1971.3	56.8
1.0	57.1	108.9	65.2	2022.9	50.5
1.8	43.9	80.4	54.0	1898.1	44.3
3.2	29.1	31.4	46.7	1896.1	39.8
5.6	17.5	19.0	39.5	1801.6	47.1
10.0	10.9	19.1	31.5	1737.1	45.0
17.8	7.9	7.7	21.9	1678.3	37.0
31.6	6.0	4.4	13.4	1557.0	34.5
56.2	4.7	2.8	3.6	1488.0	32.1
100.0	3.9	2.3	2.9	1438.6	29.6

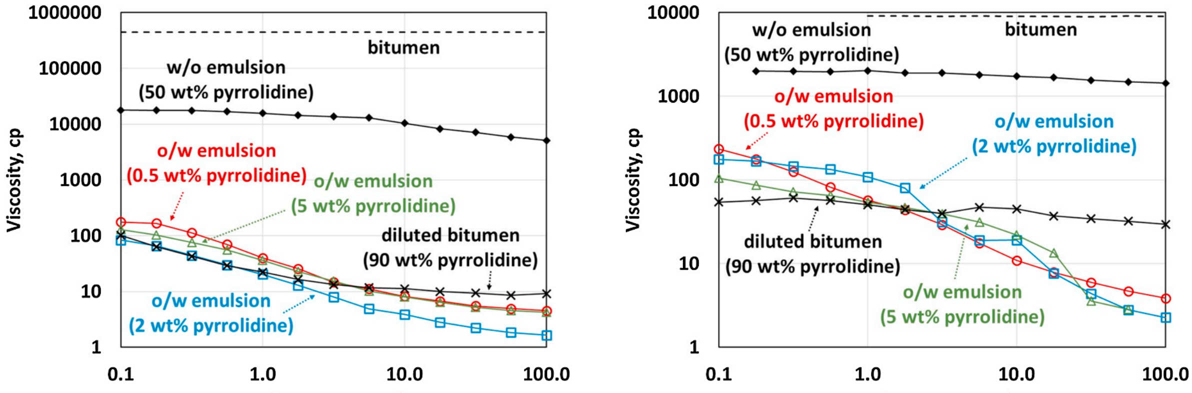
c. Temperature 353 K

Pyrrolidine concentration Emulsion type Shear rate [1/sec]	0.5 wt% o/w Viscosity [cp]	2 wt% o/w Viscosity [cp]	5 wt% o/w Viscosity [cp]	50 wt% w/o Viscosity [cp]	90 wt% dilution Viscosity [cp]
0.1	53.5	74.5	25.7	540.0	46.6
0.2	37.1	62.3	22.0	518.6	43.8
0.3	30.4	50.0	19.3	513.2	33.7
0.6	25.8	38.4	17.3	478.5	29.2
1.0	22.2	29.2	14.1	418.0	30.2
1.8	18.7	23.0	12.5	365.8	29.1
3.2	15.6	16.5	9.3	309.1	27.0
5.6	12.3	13.3	8.4	264.6	24.8
10.0	8.3	10.0	6.0	225.6	23.7
17.8	6.3	5.7	4.9	193.0	22.9
31.6	5.3	4.4	4.4	164.3	22.5
56.2	4.8	2.8	4.0	136.4	22.4
100.0	4.0	2.6	3.8	132.5	22.0

[a] Measurement was impossible due to the torque limit of the rheometer.

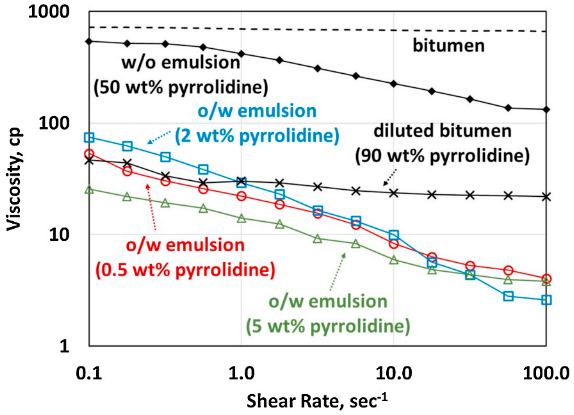
emulsion were measured at 298 K, 323 K and 353 K for selected emulsion samples at 7:3 WOR and 1000 ppm salinity. Then, the main results with pyrrolidine were compared with the previously published data with two other organic alkalis, DEA and TETA, for the same bitumen as the bitumen used in this research. Conclusions are as follows:

- It was possible to create o/w emulsions by adding a small amount of pyrrolidine to Athabasca bitumen and NaCl brine. Results showed that o/w emulsions appeared at low pyrrolidine concentrations (below 20 wt% and as low as 0.5 wt%) and low salinities (0 and 1000 ppm). As pyrrolidine concentration increased, w/o emulsions appeared. A single-phase diluted bitumen was observed at 90 wt% pyrrolidine in the aqueous solution.
- Single-phase o/w emulsions, which maximize the utilization of aqueous phase as a bitumen carrier, were observed at various conditions at 373 K: (1) for WOR 9:1, 1–5 wt% pyrrolidine at 1000 ppm, (2) for WOR 7:3, 0.5–5 wt% pyrrolidine at 0 and 1000 ppm, and (3) for WOR 5:5, 1–10 wt% pyrrolidine at 0 ppm. For samples of 0.5 wt% pyrrolidine with WOR 7:3 at 1000 ppm, a single-phase o/w emulsion was observed for all temperatures from 298 K to 373 K.
- The o/w emulsions created in this research were much less viscous than the original bitumen. They were 4 to 6 orders of magnitude less



a. Temperature 298 K

b. Temperature 323 K



c. Temperature 353 K

Fig. 6. Viscosity of o/w emulsions (0.5, 2, and 5 wt% pyrrolidine in aqueous phase), w/o emulsions (50 wt% pyrrolidine in aqueous phase), diluted bitumen (90% pyrrolidine in aqueous phase) at three different temperatures (298 K, 323 K, and 353 K). Salinity and water-oil-ratio were fixed at 1000 ppm and WOR 7:3. The viscosity of original bitumen (dot-line) is also plotted to show the viscosity reduction by creating o/w emulsions.

Table 5
Organic alkali properties.

Alkali	Formula	Molecular weight [g/mol]	Hansen solubility parameter [72]		
			Dispersion	Polarity	Hydrogen
Diethylamine (DEA)	$C_4H_{11}N$	73	14.9	2.3	6.1
Pyrrolidine	C_4H_9N	71	17.9	6.5	7.4
Triethylenetetramine (TETA)	$C_6H_{18}N_4$	146	Not available		

viscous at 298 K, 2–3 orders of magnitude less viscous at 323 K, and 1–2 orders of magnitude less viscous at 353 K.

- Pyrrolidine was superior to DEA and TETA as cosolvent for o/w emulsification of the bitumen studied. Analysis of the results indicates that it is important to consider the affinity of the organic alkali for bitumen for o/w emulsification at a wide range of temperatures. Important factors for this purpose include the polarity, the steric effect that affects the molecular shape, and the Hansen solubility parameter of the organic alkali to be used.

Acknowledgements

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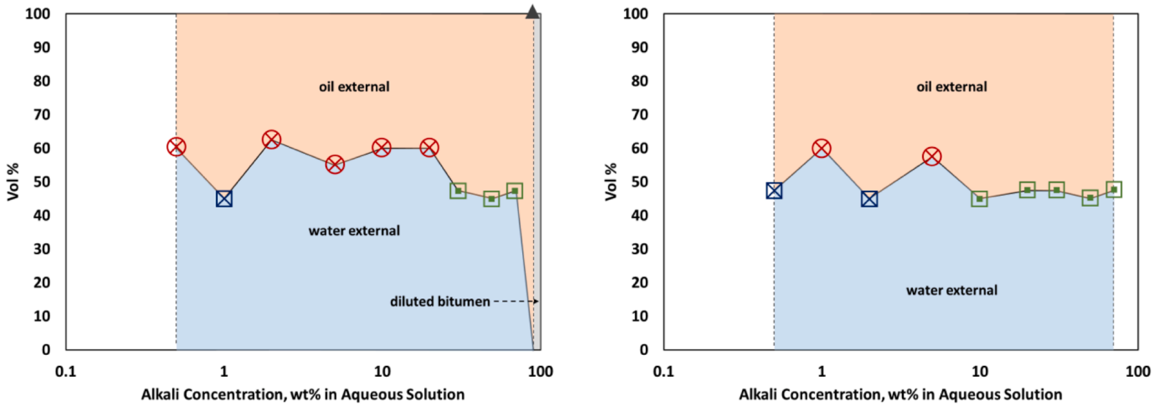
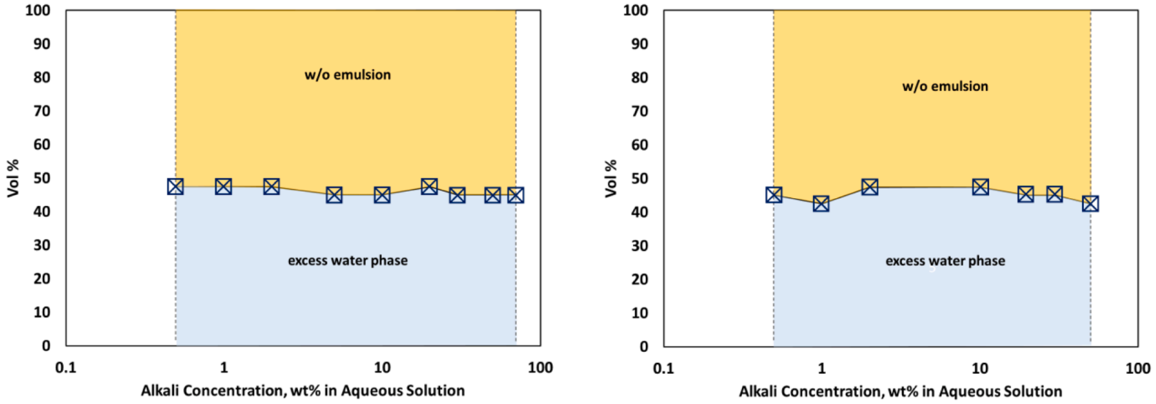
A. Emulsion phase behavior with TETA [49]

See Figs. A1–A3.



a. WOR 5:5, Salinity: 0 ppm

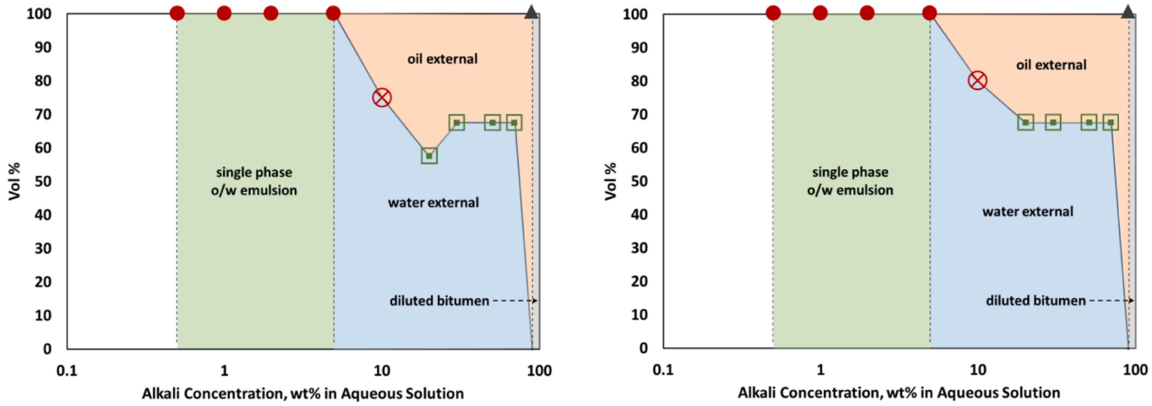
b. WOR 5:5, Salinity: 1,000 ppm



c. WOR 5:5, Salinity: 30,000 ppm

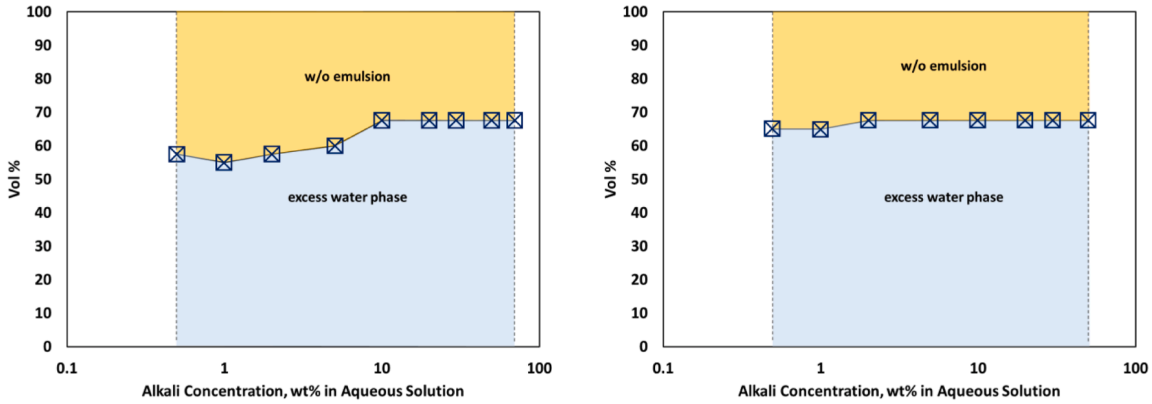
d. WOR 5:5, Salinity: 100,000 ppm

Fig. A1. 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 0.5 wt% and 2.0 wt%. At 1000 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.



a. WOR 7:3, Salinity: 0 ppm

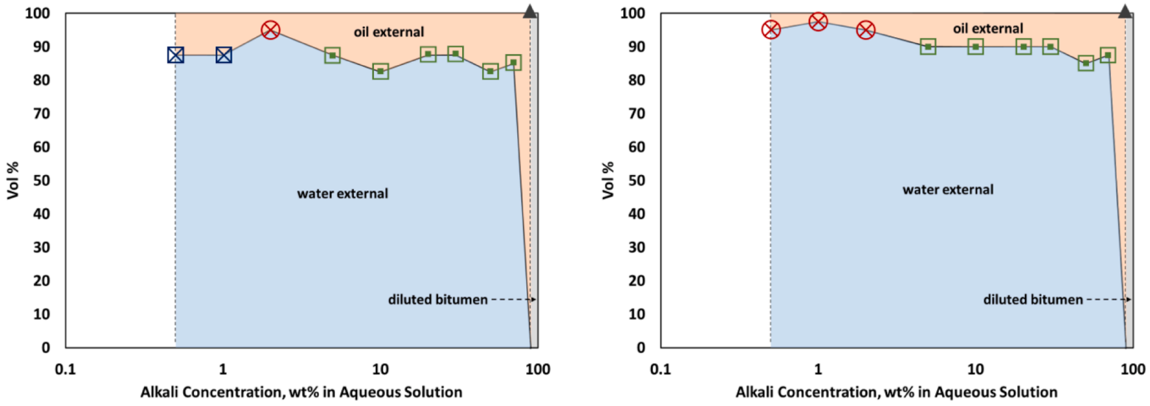
b. WOR 7:3, Salinity: 1,000 ppm



c. WOR 7:3, Salinity: 30,000 ppm

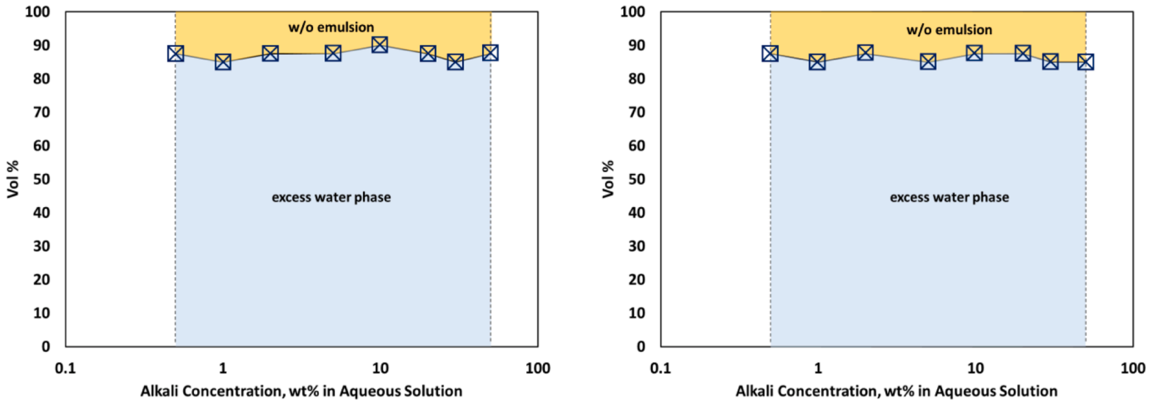
d. WOR 7:3, Salinity: 100,000 ppm

Fig. A2. 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 wt%, o/w emulsions with excess oil phase were observed at 0 ppm and 1000 ppm. From 20 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.



a. WOR 9:1, Salinity: 0 ppm

b. WOR 9:1, Salinity: 1,000 ppm



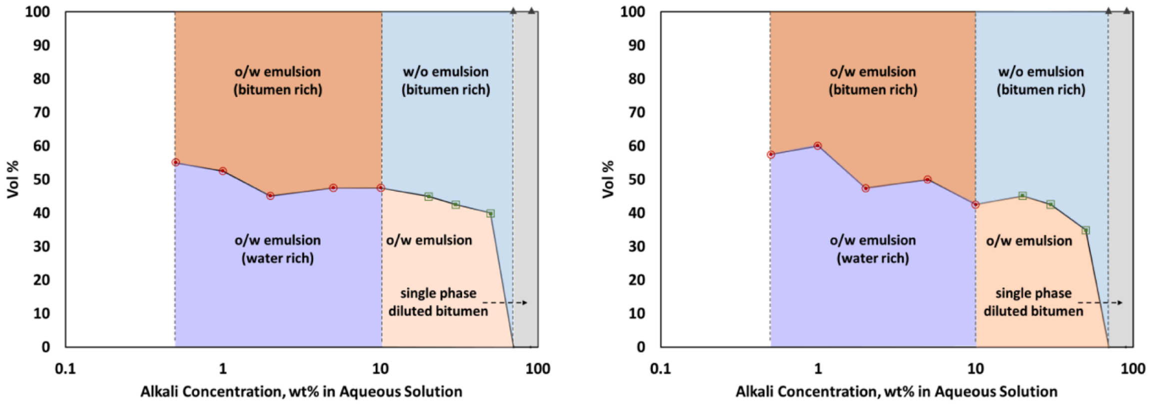
c. WOR 9:1, Salinity: 30,000 ppm

d. WOR 9:1, Salinity: 100,000 ppm

Fig. A3. 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. At 1000 ppm, o/w emulsions with excess oil phase 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 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.

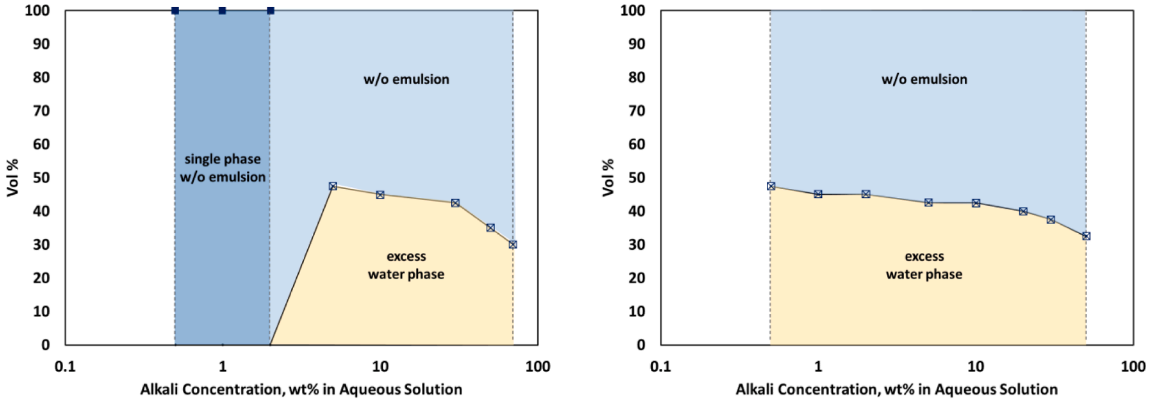
B. Emulsion phase behavior with DEA [50]

See Figs. B1–B3.



a. WOR 5:5, Salinity: 0 ppm

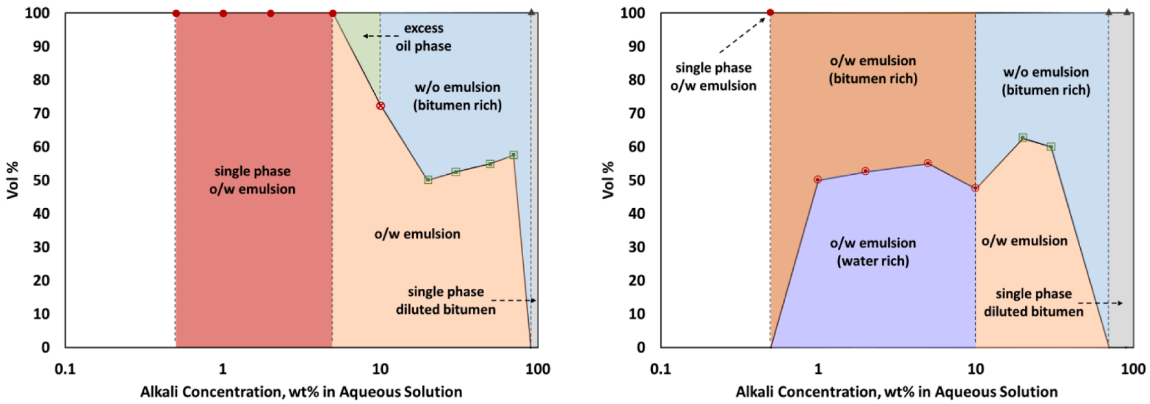
b. WOR 5:5, Salinity: 1,000 ppm



c. WOR 5:5, Salinity: 30,000 ppm

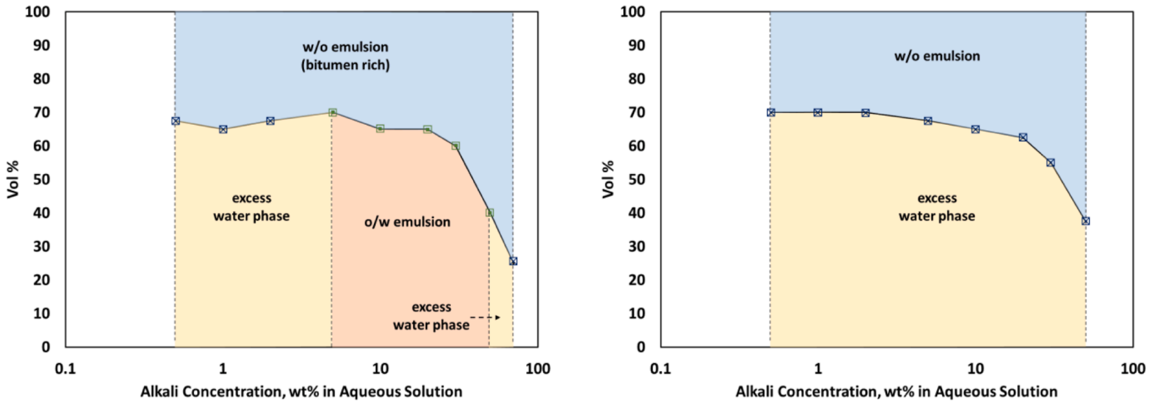
d. WOR 5:5, Salinity: 100,000 ppm

Fig. B1. 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 and 1000 ppm, two o/w emulsions (bitumen-rich and water-rich) were observed up to 10 wt%. W/o and o/w emulsions were observed from 20 wt%. Note that this w/o emulsion contained almost all bitumen. For 30,000 ppm samples, a single phase w/o emulsions were observed at low DEA concentration up to 2.0 wt%. Otherwise, w/o emulsions with an excess water-rich phase were observed. For 100,000 ppm samples, w/o emulsions with an excess water-rich phase were observed. ■: a single phase water-in-oil emulsion. ▲: a single phase diluted bitumen. ⦿: oil-in-water emulsions (bitumen rich) with oil-in-water emulsions (water rich). ▣: water-in-oil emulsions (bitumen rich) with oil-in-water emulsions (water rich). ⊠: water-in-oil emulsions with excess water phase.



a. WOR 7:3, Salinity: 0 ppm

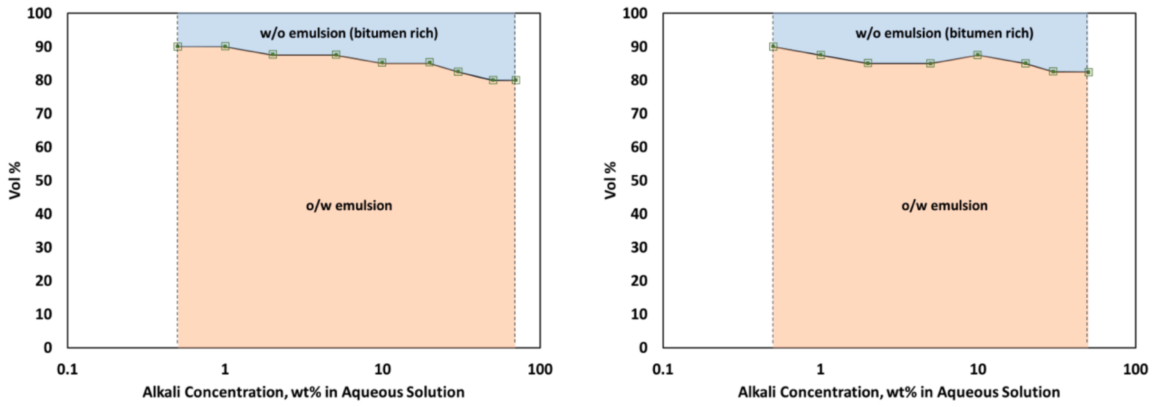
b. WOR 7:3, Salinity: 1,000 ppm



c. WOR 7:3, Salinity: 30,000 ppm

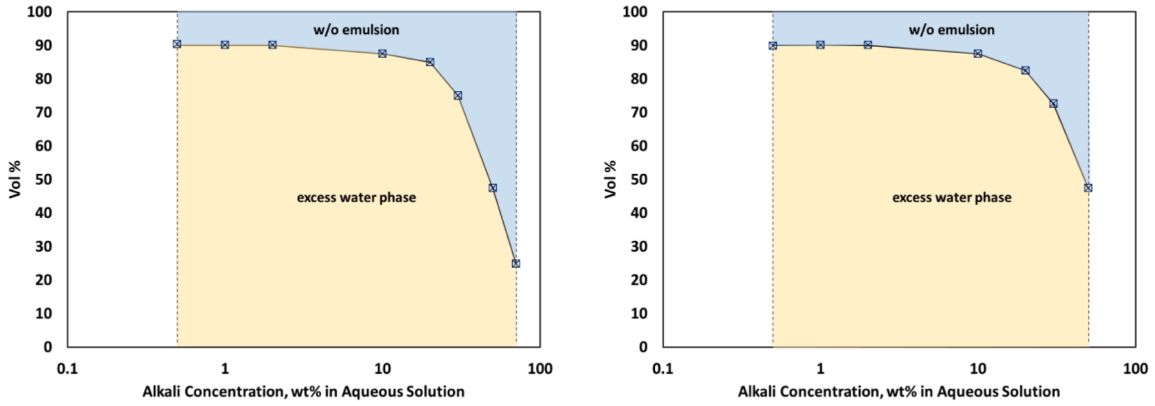
d. WOR 7:3, Salinity: 100,000 ppm

Fig. B2. 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 at low DEA concentrations at salinities 0 ppm and 1000 ppm. At 0 ppm, o/w emulsion phase with an excess oil phase was observed at 10 wt%. At 1000 ppm, two o/w (bitumen-rich and water-rich) emulsions were observed up to 10 wt% DEA. Two phase w/o – o/w emulsions were observed from 20 wt% to 70 wt% at both 0 ppm and 1000 ppm. Note that this w/o emulsion contained almost all bitumen. For 30,000 ppm samples, w/o emulsion with o/w emulsion or excess water-rich phase were observed. For 100,000 ppm samples, w/o emulsions with excess water-rich phase were observed. ●: a single phase oil-in-water emulsion. ▲: a single phase diluted bitumen. ⊗: oil-in-water emulsions with excess oil phase. ⊙: oil-in-water emulsions (bitumen-rich) with oil-in-water emulsions (water-rich). ▣: water-in-oil emulsions (bitumen-rich) with oil-in-water emulsions (water-rich). ☒: water-in-oil emulsions with excess water phase.



a. WOR 9:1, Salinity: 0 ppm

b. WOR 9:1, Salinity: 1,000 ppm



c. WOR 9:1, Salinity: 30,000 ppm

d. WOR 9:1, Salinity: 100,000 ppm

Fig. B3. 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. Two phase w/o – o/w emulsions were observed for 0 ppm and 1000 ppm samples. This w/o emulsion contains almost all bitumen. For 30,000 ppm and 100,000 ppm samples, w/o emulsions with excess water-rich phase were observed. ▣: water-in-oil emulsions (bitumen rich) with oil-in-water emulsions (water rich). ☒: water-in-oil emulsions with excess water phase.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2019.02.123.

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