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Bitumen Extraction from Oil Sands via Targeted Emulsified Solvent Injection (TESI)

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Abstract

This work introduces a Targeted Emulsified-Solvent Injection (TESI) process for extracting bitumen from oil sands. In TESI, a solvent is emulsified near the emulsion phase inversion point (PIP), where the interfacial tension and the emulsion stability are very low. This allows the solvent to be easily emulsified and then deposited onto the bitumen-coated porous media (under lower shear conditions, where the emulsion breaks), mixing with bitumen, decreasing bitumen viscosity, and enabling mobilization and diluted bitumen recovery. The design of the surfactant-solvent formulation was guided by the Hydrophilic-Lipophilic-Difference and Net-Average-Curvature (HLD-NAC) frameworks. The HLD-NAC was used to identify a formulation with less than 1% surfactant exhibiting ultralow interfacial tension ($\sim 10^{-3}$ mJ/m²), at the PIP, where HLD = 0. This formulation was injected into columns packed with bitumen-coated sands at varying salinities and water-to-solvent ratios. Using optimal conditions, bitumen recoveries of up to 83% can be obtained at room temperature, without the need for steam or high-pressure injection, a condition suitable for intermediate-depth reservoirs. The effluent emulsion of diluted bitumen can be gravity-separated, allowing for the recycling of the aqueous solution containing the surfactant. The recovery curves were modeled using a continuous stirred tank reactor (CSTR) model coupled with a Capillary number model for thin viscous films that allowed the prediction of effluent diluted bitumen viscosities and an estimation of the pressure drops in the column that were consistent with experimental observations.

Keywords: bitumen; microemulsions; extraction; surfactants; HLD; NAC

1. Introduction

Bitumen extraction from Canadian oil sands is accomplished using two methods: surface mining for reservoir depths below 75 m, and steam injection for depths above 300 m, with a reservoir thickness of 10 m or more [1]. This creates an unexploited intermediate depth region for which there is no suitable extraction technology, and where a surfactant-based chemical enhanced oil recovery (cEOR) could fill the gap.

Chemical EOR has received ample attention and has been implemented from light to heavy crude oils; some approaches involve the use of aqueous solutions of alkalis, surfactants and polymers to reduce the interfacial tension (IFT) between the crude oil and the displacing fluid (aqueous phase) and to improve the sweep efficiency by increasing the viscosity of the displacing fluid to reduce its mobility relative to the oil, known as mobility control approach [2]. Other chemical EOR approaches use stable oil-in-water (O/W) macroemulsions to selectively plug the larger pore throats to control the mobility of



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the displacing aqueous phase towards the less permeable areas and enhance the sweeping efficiency of the crude oil [3–5].

McAuliffe [3] was amongst the first to show that dilute stable macroemulsions can be used to effectively reduce both the permeability and water mobility of a reservoir by conducting flooding experiments on an array of cores. The emulsions effectively plugged the more permeable cores, diverting the flow towards the less permeable ones. More recently, Guillen et al. [4] conducted a similar experiment with two parallel sandstone cores, reaching the same conclusion. McAuliffe also highlighted the advantage of stable macroemulsions in achieving deeper penetration into the reservoir. Mandal et al. [5] injected emulsion slugs after waterflooding in a sand pack initially saturated with light crude oil, and attained 20% incremental recovery over waterflooding.

Different from the stable emulsion approaches mentioned above, the intent of this work on Targeted Emulsified Solvent Injection (TESI) is to introduce an emulsified solvent formulated near the surfactant phase inversion point, where the oil-water interfacial tension (IFT or γ_{o-w}) is at or near ultralow conditions such that the emulsion can be maintained during injection (under shear) but then breaks in the lower shear environment of the porous media. Once the solvent is released in the porous media, the solvent is expected to mix (to a certain extent) with the bitumen of the formation and reduce its viscosity. The surfactant formulation is also expected to produce low or ultralow IFT with the solvent-diluted bitumen produced in the formation, reducing the capillary forces retaining this diluted bitumen to the porous media. At that point, the diluted bitumen (now behaving as a light crude oil) is expected to follow the well-established mechanisms of surfactant-based enhanced oil recovery [6–8].

Sarbar et al. [9] extracted bitumen from Athabasca oil sands using microemulsions (μ Es) containing solubilized solvent (at a water-to-solvent ratio (W/SI) of 2.2), and in some cases emulsified solvent formulations (the latter being a similar approach to that used in this work). The authors used a surfactant concentration (C_s) of 9 wt%, with 2-butoxyethanol as cosurfactant, and flushed the formulations through packed oil sand columns, obtaining recoveries of 71% with toluene and AOT (dioctyl sulfosuccinate surfactant), and over 85% with SDBS (sodium dodecylbenzene sulfonate). The authors used an approximate solvent-to-bitumen ratio of 6. Sarma et al. [10] extracted heavy oil (10.5 Pa·s) from sand packs using solvent-in-water emulsions with gas condensate (W/SI = 2.3–9.0) and nonionic surfactant (C18E2, diethylene glycol mono octadecyl ether) at C_s = 1–2%. They injected approximately 2 pore volumes (PV) of the formulation, followed by chase water flooding, and achieved 40 to 60% recoveries. Sarma and colleagues emphasized that mobility control to minimize viscous fingering, reduction of the oil viscosity by solvent dilution, and IFT reduction are all important factors. Mohammadzadeh et al. [11] used a proprietary mixture of solvents, alkali and surfactants capable of reducing the IFT to 0.03 mJ/m² and reducing the residual oil saturation from 94% to 68% for heavy oil (12.5 Pa·s) at room temperature.

Although the literature discusses the complex interconnection among formulation, heavy oil/bitumen viscosity and chemistry, capillary phenomena, and hydraulics, there is no framework connecting these pieces. In addition to introducing TESI, this work also explores a highly simplified mixing tank model that concentrates on tracking an “instantaneous” solvent-bitumen mixing and how the interplay of viscosity, IFT reduction, and superficial velocity results in diluted bitumen removal. While the model reproduces the experimental trends and helps identify desirable operation conditions, its limitations (particularly on mass and momentum transport considerations) and opportunities for improvement are discussed in more detail.

2. Model Development

2.1. Surfactant-Oil-Water (SOW) Phase Behavior Prediction with the HLD-NAC Model

The Hydrophilic-Lipophilic-Difference (HLD) + Net-Average Curvature (NAC) model has been used as an equation of state to predict SOW properties (e.g., IFT, solubilization capacity, contact angles, phase diagrams) starting from formulation conditions such as type of surfactant, oil, salinity, and temperature [12,13]. For the specific case when the oil is solvent-diluted bitumen, the naphthenic acid (NA) fraction in bitumen behaves as a polar oil (partly as an oil and partly as a surfactant), which requires the incorporation of this polar oil behavior in the HLD-NAC model [14,15]. Although this has required complex parameter determination and fitting in the past, Tan and Acosta introduced a protocol for the prediction of SOW phase behavior of nonionic surfactant mixtures and an oil mixture of non-polar oil (heptane) and polar oil (clove oil) [16]. A set of chapters of a book on HLD-NAC reviews the origin and validation of the terms in the HLD equation, and the mixing rules used to calculate mixed surfactant and mixed oil behavior [12,17,18]. The algorithm of Figure 1 is an adaptation of Tan and Acosta's algorithm to anionic surfactant mixtures. The algorithm of Figure 1 is later used to predict the interfacial tension (IFT) of diluted bitumen with a mixture of AOT and sodium oleate (anionic surfactants).

Block BA1 of Figure 1 introduces the inputs of the model: T is the temperature of the system (25 °C for the systems of this work); C_{c1} and C_{c2} are the characteristic curvatures (C_c) of surfactants 1 (AOT), and 2 (sodium oleate, or SOle); $C_{c_{po}}$ is the C_c of the naphthenic acid (NA, polar oil) present in bitumen; $EACN_{np}$ is the equivalent alkane carbon number (oil hydrophobicity) of the non-polar oil (a mixture of 67 vol% cyclohexane, $EACN = 3$, and 33 vol% bitumen, $EACN = 11$ [14]; thus, $EACN_{np} = 3 \times 0.67 + 11 \times 0.33 = 5.6$ [18]); $EACN_{po}$ is the EACN of naphthenic acid (estimated using the octanol-water partition, $\log P = 5.5$, and density = 0.98 g/mL in a shortcut method for EACN estimation [18]); $(v_s/a_s)_1$ and $(v_s/a_s)_2$ are the surfactants' molecular volume to interfacial area (neck area) ratio; k is the EACN constant; α_T is the temperature constant (0.01 °C⁻¹ [17]); L is the surfactant tail parameter, that for surfactant mixtures can be estimated using the linear mixing rule $L = x_{s1}L_1 + (1 - x_{s1})L_2$, where x_{s1} is the molar fraction of surfactant 1 mixed with surfactant 2; S is the salinity of the system, noted as % NaCl in this work ($S = 1\%$ means 1 g of NaCl/100 mL of aqueous solution, or 0.17 M NaCl); K_m is the partition coefficient of the polar oil between the surfactant layer and the bulk oil phase; q_{max} is the maximum ratio between the moles of polar oil (naphthenic acid) to moles of surfactants (surfactants 1 + surfactants 2) at the interface; C_{s1} and C_{s2} are oil-equivalent molar concentrations (surfactant moles/volume of oil phase) of surfactants 1 and 2; $C_{i,po}$ is the initial molar concentration of the polar oil (naphthenic acid) in the oil; MW_1 , MW_2 , and MW_{po} are the molecular weights of surfactants 1, 2 and of the polar oil; ρ_1 , ρ_2 and ρ_{po} are the densities of surfactants 1, 2 and of the polar oil; E_r is the interfacial rigidity of the system, reflecting the surfactant-surfactant interactions, reported in $K_B T$ (Boltzmann's constant times temperature, thermal energy units); finally, ξ is the characteristic length of the μE , interpreted as the maximum solubilization radius that the SOW system can achieve.

The prediction of the characteristic length (ξ) has recently become possible through the overlap factor theory (OFT) [12], and its application to mixtures with polar oils [16]:

$$\xi = \sum_{i=1}^n \left(\frac{x_i}{1.64 \text{ \AA} \cdot \exp \left(5 \cdot \frac{(v_t/a_s)_i}{\sqrt[3]{V_{m_{oil}}}} \right)} \right)^{-1} \exp(0.84 \cdot (HLD_{po} - HLD_{np})) \quad (1)$$

where x_i is the molar fraction of surfactant "i", $(v_t/a_s)_i$ is the ratio between surfactant tail volume and the surfactant area per molecule, $V_{m_{oil}}$ is the molar volume of the oil

($V_{m, oil} = 240 \text{ \AA}^3$ estimated for 2 parts cyclohexane and 1 part bitumen with an average MW of 500 g/mol and a density of 1 g/mL). HLD_{po} and HLD_{np} are the HLDs of the system considering the presence and absence of polar oil, respectively. The values and sources of the inputs are listed in Table 1.

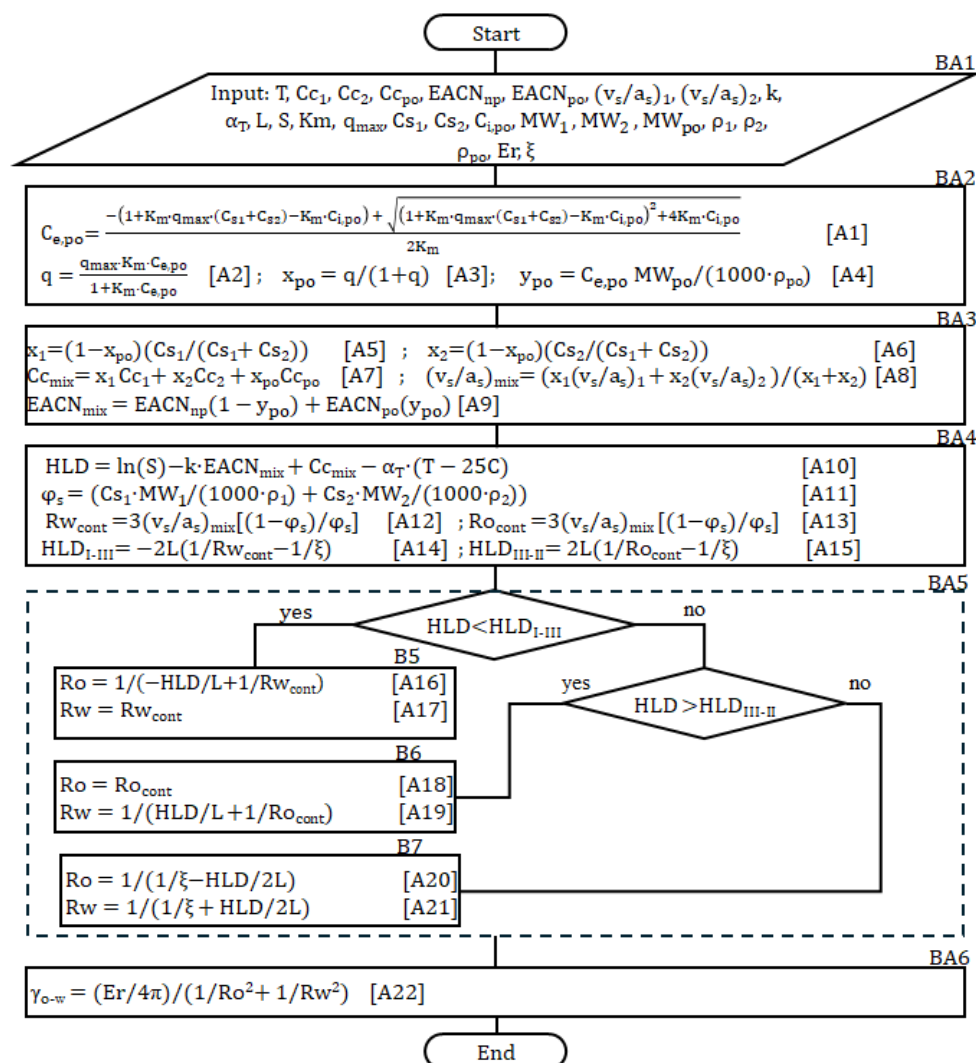


Figure 1. Bifunctional HLD-NAC algorithm for mixtures of anionic surfactants (AOT and sodium oleate) with a polar oil (naphthenic acid). Adapted from the bifunctional algorithm for nonionic surfactants of Tan and Acosta [16].

Block BA2 concentrates on determining the proportion of the polar oil (naphthenic acid, NA) that segregates towards the oil-water interface, and the proportion that stays in the bulk oil. To this end, the Langmuir adsorption equation $q = q_{max} \cdot K_m \cdot C_{e,po}/(1 + K_m \cdot C_{e,po})$ is used, where q represents the moles of polar oil segregated to the interface per mole of total surfactant. The total surfactant, in this case, is the mixture of surfactants 1(AOT) and 2 (SOle). $C_{e,po}$ is the concentration of naphthenic acid in the bulk oil after the segregation process reaches equilibrium. Equation [A1] calculates $C_{e,po}$ after combining the Langmuir adsorption isotherm with a mass balance equation for polar oil, considering the initial concentration of the polar oil before the segregation occurs ($C_{i,po}$) and the oil-equivalent surfactant concentrations (C_{s1} and C_{s2}). With the value of $C_{e,po}$, Equation [A2] calculates “ q ”. With “ q ”, the molar fraction of the polar oil that is segregated to the interface (x_{po}) is calculated using Equation [A3]. The molar concentration of the polar oil in the bulk $C_{e,po}$ is then turned into a volume fraction (y_{po}) using Equation [A4].

Block BA3 concentrates on obtaining the main HLD parameters: the characteristic curvature of the surfactant and polar oil mixture ($C_{c_{mix}}$), reflecting the hydrophilic (negative C_c) or hydrophobic (positive C_c) tendencies of the surfactant system; and the EACN of the oil mixture (higher positive EACN meaning a more hydrophobic oil). To this end, Equations [A5] and [A6] calculate the molar fractions of surfactants 1 (x_1) and 2 (x_2), respectively, but considering the molar fraction of polar oil (x_{po}). Equation [A7] uses a linear molar-based mixing rule to determine $C_{c_{mix}}$ and the C_c of the individual components. The use of a linear mixing rule has been found suitable when mixing surfactants of the same charge (anionic-anionic in this case), and when mixing surfactants and polar oils [17,19]. Equation [A9] uses a volume-based linear mixing rule [20] to find the EACN of the mixture. Equation [A8] calculates the volume to surface area for the mixed surfactant systems, excluding the polar oil, which segregates near the oil-water interface without introducing additional interfacial area [19,21,22].

Block BA4 concentrates on determining the HLD of the SOW system using Equation [A10]. The HLD serves as an indicator of the hydrophilic (negative) or hydrophobic (positive) nature of the entire SOW system. In this work, we undertook salinity (S) scans to obtain different interfacial tensions (γ_{o-w}), and therefore, Equation [A10] produces one HLD value for each salinity used; this HLD will be negative for low salinities and positive for high salinities. This block also introduces two transition HLDs; the first transition is at HLD_{I-III} (Equation [A14]), whereby if HLD of the system is more negative than HLD_{I-III} , then the system produces micellar type or Type I (oil-in-water) μ Es; the second transition is at HLD_{III-II} (Equation [A15]), whereby if HLD of the system is more positive than HLD_{III-II} , then the system produces reverse micelles or Type II (water-in-oil) μ Es; systems in between these transitions produce bicontinuous Type III μ Es. These transition boundaries are predicted by the NAC model utilizing the two-state model, whereby the shape and size of μ Es can be described considering one state where oil is solubilized (with solubilization radius $R_o = 3 \times \text{volume of oil solubilized} / \text{surfactant interfacial area}$) in a water-continuous phase, and a second state where water is solubilized (with solubilization radius R_w) in an oil-continuous phase. The NAC establishes two curvatures to describe shape and size: one is the net curvature (H_n) that represents the area-averaged curvature of the interface, and the average curvature (H_a) that represents the inverse of the radius of a sphere that has the same volume-to-area ratio as the μ E, a radius that reflects the μ E size (ξ_H) [12]:

$$H_n = \left(\frac{1}{R_o} - \frac{1}{R_w} \right) = -\frac{HLD}{L} \quad (2)$$

$$H_a = \frac{1}{2} \left(\frac{1}{R_o} + \frac{1}{R_w} \right) = \frac{1}{\xi_H} \quad (3)$$

For systems where $HLD < HLD_{I-III}$, water is the continuous phase and the solubilization radius of water, noted as $R_{w_{cont}}$ for this case, is calculated using Equation [A12]. For systems where $HLD > HLD_{III-II}$, oil is the continuous phase and the solubilization radius of oil, noted as $R_{o_{cont}}$ for this case, is calculated using Equation [A13]. Equation [A11] calculates the volume fraction of the surfactant, ϕ_s , which is approximately the same in the aqueous and the oil phase considering that the algorithm of Figure 1 was originally developed for water-to-oil volume ratios (WOR) of 1; however, for relatively small ϕ_s (less than 1% in the aqueous phase in this work), the model can be extrapolated to extreme WORs because the continuous phase solubilization radius of oil ($R_{o_{cont}}$) and water ($R_{w_{cont}}$) are much greater than the characteristic length (ξ), rendering the terms $1/R_{o_{cont}}$ and $1/R_{w_{cont}}$ negligible in comparison with $1/\xi$, which is used to calculate the Type I-III-II μ E transitions.

The purpose of the dashed section of Figure 1 is to calculate R_o and R_w for a given HLD value. Block BA5 calculates R_o (Equation [A16]) from Equation (2) for Type I μ Es,

setting R_w as $R_{w\text{cont}}$ (Equation [A17]). Block BA6 calculates R_w (Equation [A18]) from Equation (2) for Type II μEs , setting R_o as $R_{o\text{cont}}$ (Equation [A19]). Block BA7 calculates R_o (Equation [A20]) and R_w (Equation [A21]) for Type III μEs by solving Equation (2) and Equation (3) simultaneously, and setting ξ_H , the μE size, as the characteristic length of the system (ξ) that, as indicated before, is the maximum solubilization or the maximum value that ξ_H can reach.

Finally, block BA8 predicts the interfacial tension of the system (γ_{o-w}) using Equation [A22] and the values of R_o and R_w obtained for each HLD at a given salinity (S). The values of these predicted IFTs will be compared with experimental values.

Table 1. Input table for the bifunctional HLD-NAC algorithm of Figure 1 for anionic surfactants sodium dioctyl sulfosuccinate (Aerosol-OT or AOT) and sodium oleate (SOle) in the presence of cyclohexane (CHX)-diluted bitumen containing naphthenic acid (NA, a polar oil).

Parameter	Value	Notes
C_{c1} (AOT)	+2.5	From the HLD-NAC database [17]
C_{c2} (SOle)	−1.7	From the HLD-NAC database [17]
$C_{c\text{po}}$ (NA)	+3.8	From Perez-Franco and Acosta [15]
EACN_{np} (CHX/B = 2)	+5.6	Calculated considering EACNs of 11 for bitumen (B) [14] and 3 for cyclohexane (CHX) [18], and a 2/1 volume ratio.
EACN_{po} (NA)	3.7	From the shortcut method [18]
K	0.16	From the HLD-NAC database [17]
$\alpha_T, (^{\circ}\text{C})^{-1}$	0.01	From the HLD-NAC database [17]
$K_m, (\text{mol/L})^{-1}$	9	From Perez-Franco and Acosta [15]
q_{max} (mol polar oil/mol surf)	$C_{i,\text{po}}/(C_{s1} + C_{s2})$	Value can range from 0.6 to 10 [16]
$(v_s/a_s)_1, \text{\AA}$	6.1	From the HLD-NAC database [17]
$(v_s/a_s)_2, \text{\AA}$	12	From the HLD-NAC database [17]
$(v_t/a_s)_1, \text{\AA}$	4.1	From the HLD-NAC database [17]
$(v_t/a_s)_2, \text{\AA}$	12	From the HLD-NAC database [17]
$L_1, L_2, \text{\AA}$	10, 29	Estimated as 1.2 times tail length [17]
$MW_1, MW_2, MW_{\text{po}}$ (g/mol)	444, 304, 250	From the HLD-NAC database [17], and for NA estimated from its acid number
$\rho_1, \rho_2, \rho_3, \text{g/mL}$	1.08, 1.05, 0.98	From the HLD-NAC database [17]
C_{s1} (AOT), mol/L	0.011	Set by Stammitti [23]
C_{s2} (SOle), mol/L	0.010	Set by Stammitti [23]
$C_{i,\text{po}}$ (NA), mol/L	0.02	Calculated from 1.5% Na in bitumen [14]
$S, \% \text{ NaCl}$	0.1 to 2	Salt in the aqueous phase
$Er, K_B T$	1	From Perez-Franco and Acosta [15]

2.2. Continuously Stirred Tank Reactor (CSTR) Model for Bitumen Dissolution and Removal

Earlier attempts at understanding bitumen removal in TESI using conventional capillary number (Ca) definitions and reservoir modeling considerations pointed to the dissolution of bitumen in the solvent as the controlling step of the process [23]. Figure 2 illustrates a schematic of this approach. According to the CSTR approximation, the bitumen layer deposited on the surface of the pore can be thought of as being composed of two parts, one an “unavailable” (insoluble) portion, with residual saturation (volume fraction of the total

pore volume) S_{nU} . This portion is not insoluble due to thermodynamic limitations, but rather due to the transport conditions of the process (flow, viscosity ratio, temperature, etc.) that do not provide enough time for the solvent to reach the deepest portion of the bitumen in the pore. A more comprehensive model would replace this insoluble compartment with a kinetic model of the dissolution of bitumen. The “available” bitumen portion, with residual saturation S_{nA} , is considered to mix with the emulsified solvent instantaneously. The sum of the available and unavailable saturations should lead to the total (initial) bitumen saturation ($S_{n0} = S_{nA} + S_{nU}$). Once the bitumen mixes with the solvent, a new compartment of “diluted bitumen”, or DB, is created, with a residual saturation S_{nDB} . As more emulsified solvent (in the aqueous surfactant solution) is pumped into the porous media, S_{nDB} increases (filling stage) until this residual saturation reaches a maximum residual saturation (S_{nmax}) set by the capillary conditions, reflected by a critical Capillary number (Ca_λ) that considers the viscosity ratio (λ) between the diluted bitumen and the aqueous phase. In the reservoir engineering literature, this S_{nmax} concept is equivalent to the critical saturation. Since the injection of solvent changes the viscosity of the oil and the viscosity ratio (λ), S_{nmax} changes throughout the duration of the solvent injection. As the diluted bitumen saturation reaches S_{nmax} , the diluted bitumen begins to be released from the porous media (production stage).

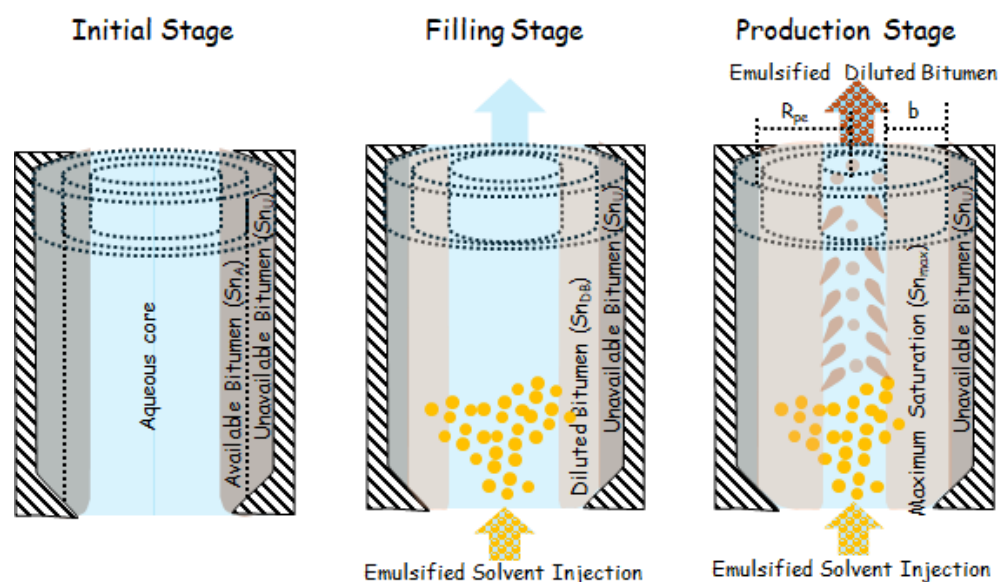


Figure 2. Schematic of the CSTR model for bitumen removal through the TESI approach. S_{n0} is the initial residual saturation of bitumen in the pore. S_{nA} is the residual saturation that is available for mixing with the emulsified solvent. S_{nU} is the residual saturation that does not mix with the solvent and is not removed from the pore. S_{nmax} is the maximum residual saturation in the diluted bitumen (DB) chamber.

The Supplementary Information File contains the mass balance for this CSTR approximation, leading to the equation for the bitumen recovery, $\%rec = 100 \cdot (1 - \exp(-(S_{nA} + S_{IPV} - S_{nmax})/S_{nmax})) \cdot S_{nA}/S_{n0}$, where S_{IPV} is the volume of solvent (fed as an emulsion in the aqueous surfactant solution), reported as pore volume of solvent injected. The CSTR model was implemented in the algorithm of Figure 3. The purpose of the algorithm is to fit bitumen recovery ($\%rec$) using the appropriate critical capillary number (Ca_{p_crit} , the Ca_λ value beyond which oil is released from the porous media) and unavailable residual saturation (S_{nU}). After achieving that fit, the algorithm proceeds to predict the viscosity of the produced diluted bitumen (μ_{DB}) and the pressure drop across the column (ΔP).

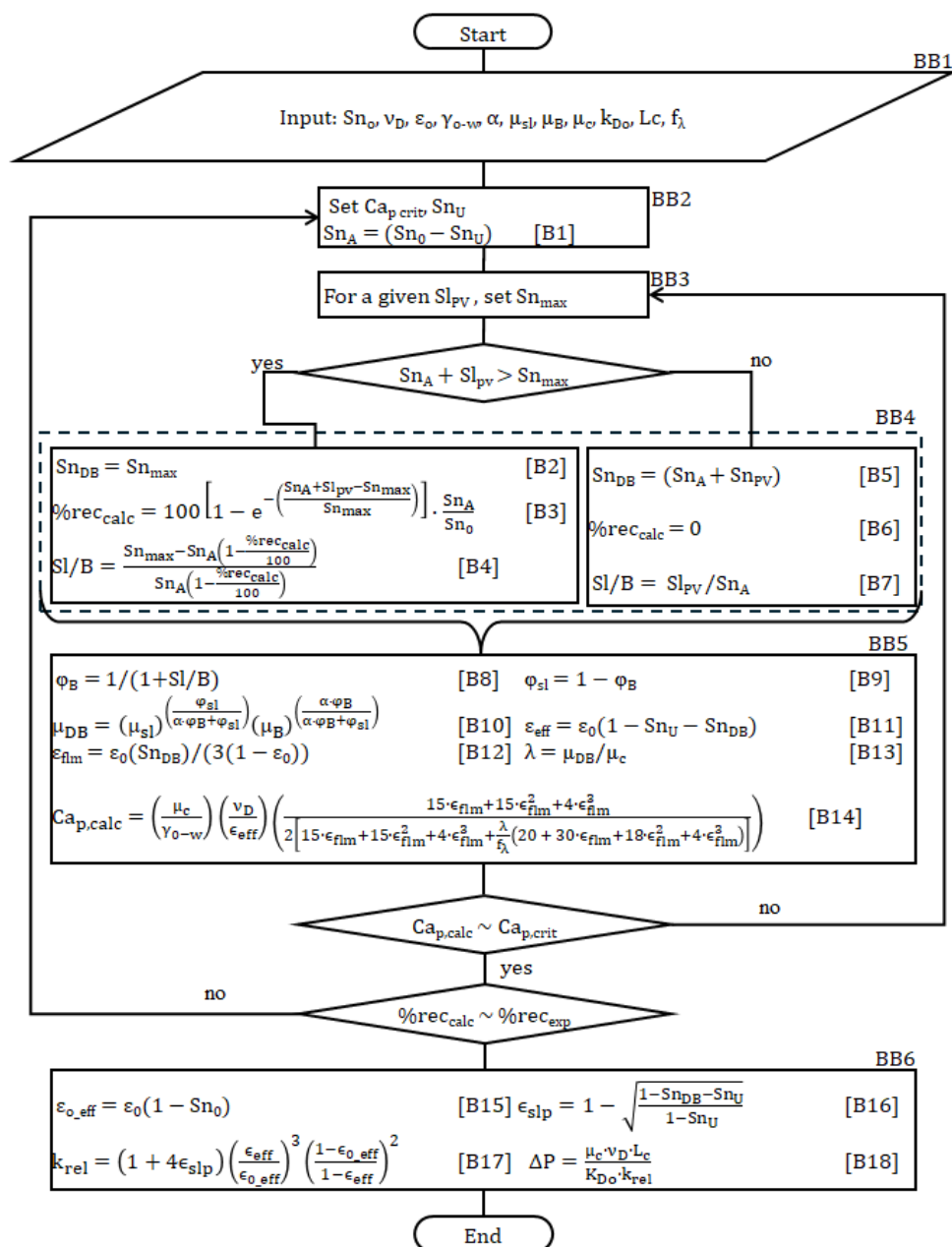


Figure 3. Algorithm for the Continuously Stirred Tank Reactor (CSTR) model for bitumen dissolution and removal.

The inputs of the CSTR algorithm (block BB1) include the initial bitumen saturation (S_{n0}), the superficial velocity of the injected emulsion (v_D , volumetric flow/column's cross-sectional area), the porosity of the packed column (ϵ_0), the oil-water interfacial tension (γ_{o-w}), the viscosities of the pure solvent (μ_{sl}), of the undiluted bitumen (μ_B), and of the continuous phase (μ_c , taken as the viscosity of the continuous phase of the emulsion, the aqueous surfactant solution) and the parameter “ α ” used in Lederer’s model [24] to relate the viscosity of diluted bitumen (μ_{DB}) with the solvent volume fraction mixed with bitumen (ϕ_{sl}); the input also includes the initial Darcy permeability of the column (k_{Do}), and the length of the column (L_c). Finally, the factor f_λ , used to obtain the particle-based calculated Capillary number ($Ca_{p,calc}$), is also set in this block.

Block BB2 sets the initial guesses for the critical capillary number ($Ca_{p,crit}$), and the unavailable saturation (S_{nU}), and Equation [B1] calculates the available saturation (S_{nA}). Block BB3 sets the initial guess of maximum saturation (S_{nmax}), which later has to be

confirmed (or reassessed) to match the previously set Ca_{p_crit} for the given solvent pore volume being considered (Sl_{PV}). If the saturation of the sum of the available saturation and the solvent pore volume is more than the maximum saturation ($Sn_A + Sl_{PV} > Sn_{max}$), then the system has entered the production stage and the % bitumen recovery ($\%rec_{calc}$) is calculated through Equations [B2] and [B3] (derived in the Supplementary File) in block BB4, followed by Equation [B4] used to calculate the solvent-to-bitumen volume ratio (Sl/B) in the produced bitumen. If the conditional is not satisfied, then the system is not yet in production; thus, there is no bitumen recovery (Equation [B6]), and the Sl/B ratio is calculated with Equation [B7].

In block BB5, the volume fraction of bitumen mixed with the solvent is calculated using Equation [B8], and the solvent volume fraction with Equation [B9]. The viscosity of the diluted bitumen (μ_{DB}) is calculated using Lederer's model [24], represented by Equation [B10]. Equation [B11] calculates the effective porosity of the system (ϵ_{eff}) by subtracting the fraction of the volume occupied by the undiluted and diluted bitumen from the total porosity. Equation [B12] calculates the diluted bitumen normalized film thickness (ϵ_{flm}) using Mehrabian's particle-based Capillary number (Ca_λ , but noted in the algorithm as Ca_p) [25], which was developed to represent how shear from a low-viscosity aqueous medium is transmitted to viscous diluted bitumen films. In Mehrabian's work, ϵ_{flm} is calculated as the ratio between the diluted bitumen film thickness and the particle radius. In this work, the film thickness ("b" in Figure 2) is estimated as the ratio between the volume of diluted bitumen (V_{DB}) and the particle area (a_p), $b \sim V_{DB}/a_p$. The particle radius (R_p) can be estimated as $R_p \sim 3V_p/a_p$, where V_p is the volume of the particle. Therefore, $\epsilon_{flm} = b/R_p \sim V_{DB}/3V_p \sim (V_{DB}/V_T)/(3V_p/V_T)$, where V_T is the total volume of the porous media. The numerator of Equation [B12] represents (V_{DB}/V_T), and the denominator represents ($3V_p/V_T$). Equation [B13] calculates the ratio between the viscosity of diluted bitumen and the viscosity of the continuous phase (λ). Equation [B14] is used to obtain the particle-based calculated Capillary number ($Ca_{p,calc}$), based on Mehrabian's particle-based Capillary number (Ca_p) [25], but modified to estimate the pore velocity as the ratio between the superficial velocity (v_D) and the effective porosity (ϵ_{eff}), and incorporating a scaling factor, f_λ , to correct the effect of viscosity ratio (λ), that was initially developed for free-falling oil-coated particles in aqueous media. This calculated capillary number, $Ca_{p,calc}$, is then compared with the set critical capillary number (Ca_{p_crit}), and if they do not match, then a new Sn_{max} is assumed in BB3, and the calcs in BB4 are repeated until $Ca_{p,calc} \sim Ca_{p_crit}$. Once the match is obtained, the calculated oil recoveries ($\%rec_{calc}$) for different solvent pore volumes (Sl_{PV}) are compared with the experimental values, and if they are far from each other, new values of Ca_{p_crit} and unavailable saturation (Sn_U) are selected in BB2.

Once the deviations between the experimental and calculated recoveries are minimized, the pressure drop (ΔP) across the column is then estimated in block BB6. Equation [B15] is used to calculate the initial effective porosity (ϵ_{o_eff}). Equation [B16] is used to calculate the lubricating film ratio (ϵ_{slp}) between the diluted bitumen film thickness "b" and the effective inner pore radius " R_{pe} ", illustrated in Figure 2, such that $\epsilon_{slp} = b/R_{pe}$. To estimate this ratio, let us imagine the pore being a cylinder where the volume of the fluid (V_{fluid} = diluted bitumen + aqueous core) is $V_{fluid} = \pi \cdot R_{pe}^2 \cdot L_p$, where L_p is the length of the pore; and where the volume of the aqueous core is $V_{core} = \pi \cdot (R_{pe} - b)^2 \cdot L_p$; then $V_{core}/V_{fluid} = (R_{pe} - b)^2/R_{pe}^2 = (1 - b/R_{pe})^2$, where the ratio of the two volumes is the ratio of their respective saturations, $V_{core}/V_{fluid} = (1 - b/R_{pe})^2 = (1 - Sn_{DB} - Sn_U)/(1 - Sn_U)$; then, isolating for $\epsilon_{slp} = b/R_{pe}$ yields Equation [B16]. The lubricating film ratio is then used in Equation [B17] to calculate the relative permeability of the continuous aqueous phase (k_{rel}). Equation [B17] incorporates the film slip term ($1 + 4\epsilon_{slp}$) from Berg et al. [26] and a factor

derived from the Kozeny-Carman equation to track how changes in the effective porosity of the media (as a result of changes in S_{nDB}) change the relative permeability to the aqueous phase. Finally, Equation [B18] applies Darcy's law to calculate the pressure drop across the column. It is important to clarify that in this work we assume that the flowing phase is the emulsified diluted bitumen in water, but despite being an emulsion, the viscosity of that flowing phase (μ_c) is taken as the viscosity of water because, contrasting with the flow of other emulsions in porous media, emulsions prepared at the phase inversion point (HLD = 0), under the conditions where the water-to-oil volume ratio (WOR) is greater than 1 (the conditions of this work), then the viscosity of the emulsion is approximately the viscosity of water [27]. It is also relevant to clarify that, since we were using a sand pack, we neglected anionic surfactant adsorption losses, which should be considered in other types of formations, such as carbonaceous reservoirs [28].

3. Materials and Methods

3.1. Chemicals, Solids and Surfaces

All the chemicals were sourced and used as received from the respective manufacturers. Toluene reagent grade (>99.5%) was obtained from Caledon Laboratory Chemicals (Georgetown, ON, Canada). Dioctyl sulfosuccinate sodium salt (AOT, >97%), oleic acid technical grade (>90%), sodium dodecyl sulfate (SDS, >99%), cyclohexane (anhydrous, 99.5%) and glycerol (>99.5%) were purchased from Sigma-Aldrich Canada (Oakville, ON, Canada). Sodium chloride biotechnology grade (>99.5%) and sodium hydroxide reagent grade (>98%) were purchased from Bioshop Canada (Burlington, ON, Canada). Anhydrous ethanol (UN1170) was acquired from Green Field Specialty Alcohols Inc. (Toronto, ON, Canada). Deionized-distilled water (DiDW) was obtained in-house using a Corning Glass Works distillation unit (Corning, NY, USA) equipped with an Ultra-High Purity deionization cartridge from Thermo Scientific Inc. (Waltham, MA, USA), reaching a surface tension of 71.24 ± 0.02 mJ/m² at 25 °C. Coker feed Athabasca bitumen was kindly donated by Syncrude Canada Ltd. (Edmonton, AB, Canada). Washed play sand was acquired from a local hardware store.

3.2. Surfactant-Oil-Water (SOW) System

The SOW system was chosen for this study, guided by the HLD-NAC framework, to produce an ultralow interfacial tension and relatively large oil solubilization capacity at low salinity and surfactant concentration. AOT was chosen since it has a large positive characteristic curvature (C_c) that reduces the amount of salt needed to achieve phase inversion. Furthermore, AOT has been employed in oil sand extraction studies [9]. Sodium oleate (SOle) was selected because of its negative C_c that counterbalances the positive C_c of AOT, but more importantly, the double bond in the middle of the oleate chain helps to disrupt the tendency of AOT to form liquid crystal structures. Cyclohexane was selected as the solvent for diluting bitumen in the column studies since it can fairly disperse bitumen components, particularly asphaltenes [29], it is not as environmentally hazardous as toluene, and it is also used in the extraction of vegetable oils. Furthermore, cyclohexane has been shown to produce minimal (if any) asphaltene precipitation, which could change the bitumen composition during extraction [30].

A main stock surfactant solution was prepared with total surfactant concentration ($C_{S_{total}}$) of 1.64% (expressed in grams of surfactant per 100 mL of aqueous phase) and surfactant mass ratio of AOT/SOle = 1.56, which corresponds to a 0.045 M equimolar mixture. The stock solution was prepared as follows. The specified mass of AOT (solid) was placed into a volumetric flask and filled halfway with DiDW. The flask was placed in an environmental incubator shaker for one hour (Orbit Environ-Shaker, Lab-Line Instruments

Inc., Melrose Park, IL, USA) set at 37 °C and 150 rpm to facilitate dissolution. Then, the required volume of oleic acid was added, followed by sodium hydroxide at 1.5% excess of the stoichiometric amount to ensure complete neutralization. Next, the flask was removed from the shaker and allowed to cool down. Finally, the volume was completed by adding DiDW slowly to avoid the formation of bubbles. The stock solution had a pH of 9.3.

For the interfacial tension (IFT) measurements, sequences of phase behavior scans were prepared varying salinity (S) and a $C_{s\text{total}}$ of 0.83% (0.023 M) to identify the optimum salinity (S^*) of the SOW system. This concentration of surfactant is enough to reach low to ultralow IFTs. Each aqueous solution was contacted at a 1:1 volume ratio with cyclohexane or bitumen diluted with cyclohexane (CHX/B) at a solvent-to-bitumen mass ratio (Sl/B) of 2.0. The vials were gently tumbled 10 times and allowed to equilibrate for a minimum of 48 h before measuring IFT. The pH of the equilibrated aqueous phases ranged from 8.7 to 8.9.

3.3. Interfacial Tensions and Viscosities

Upon equilibration, the aqueous and organic phases were separated, and the interfacial tensions (IFTs) were measured with a spinning drop tensiometer from TEMCO Inc. (model 500, Tulsa, OK, USA) at room temperature 25 ± 2 °C [31]. For each measurement, the drop shape was monitored for 1000 s, preventing excessive heating through an evaporative cooling towel.

The viscosities of CHX/B at varying Sl/B mass ratios and the aqueous phases of the equilibrated SOW systems were measured with the syringe aspiration method, which is frequently used to measure the viscosity of small blood samples, and it has been used in oil recovery studies [32,33]. This method was particularly useful for measuring the viscosities of the oil phases (<1 mL in some cases) in effluents collected from the column studies, as explained later. A series of glycerol-water mixtures was prepared in the range of 1–150 mPa·s for calibration. The viscosities of these mixtures were measured with a TA Instruments CSL2 500 Carri-Med rheometer (TA Instruments, New Castle, DE, USA). A Hamilton® MicroLiter™ syringe model 810RN (100 µL) with a 22s-gauge point style #2 needle (Hamilton Robotics, Reno, NV, USA) was calibrated using the glycerol-water mixtures. This syringe has a dead volume of 1.13 µL, which minimizes the loss of sample. The syringe was clamped to a stand, and the needle was introduced into the desired sample. The plunger was then pulled up rapidly to the 50 µL mark to generate a vacuum, and the fill-up time was recorded down to 0.01 s. Each measurement was repeated a minimum of five times to ensure reproducibility. After each experiment, the syringe was thoroughly cleaned with toluene, ethanol and acetone and allowed to air-dry. The calibration curve and the viscosities of the diluted bitumen (μ_{DB}) at room temperature, 25 ± 1 °C, are shown in Figure 4.

3.4. Oil Sand Preparation and Packing

Artificial oil sand at 10%wt. oil content was prepared in 40 g batches by coating clean and dry sieved play sand samples with bitumen. To facilitate manipulation and ensure an even coating, a bitumen sample was first diluted with toluene at Sl/B = 0.3 and mixed overnight in a wrist action shaker. The use of toluene as solvent helped prevent any possible changes in bitumen composition due to asphalthene precipitation.

Diluted bitumen was slowly added to the sand and mixed with a spatula for 15 min. The coated sand was placed under the fume hood for 48 h and periodically stirred to evaporate the toluene. This procedure was adapted from Quraishi et al. [33], who demonstrated, via multiple sampling of different sections of the batch, that the deviations in composition (from UV-VIS spectra of toluene-extracted fractions) were less than 2% of the nominal value. The 48 h required for drying was determined by periodic gravimetric measurements

(to reach a constant weight, within ± 2 g). This relatively short aging period would not reproduce oil sands exposed to surface conditions that lead to oxidation of various bitumen components, but it is still relevant to mid-zone reservoirs where weathering by air exposure is limited—this is the target formation of this work. It is also relevant to note that in our simulated oil sands, bitumen is in contact with dry sand, thereby eliminating the possibility of a connate water film that is said to facilitate the extraction of Athabasca oil sands. The lack of that film is believed to explain why Utah oil sands are difficult to extract.

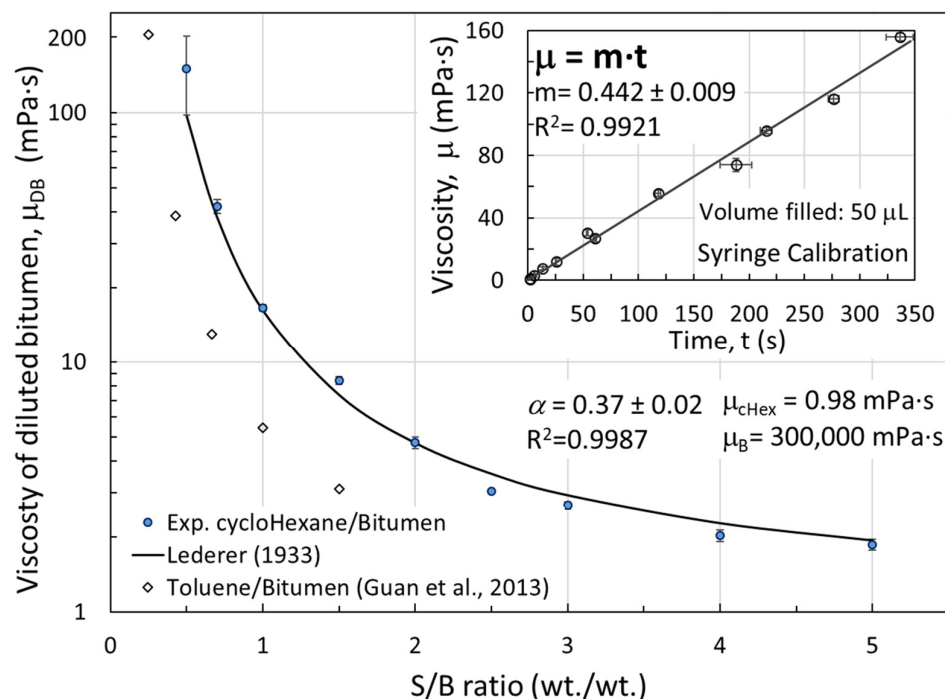


Figure 4. Viscosity of the cyclohexane/bitumen system at different ratios and corresponding fitting of Lederer's model [24]. Literature values for the toluene/bitumen system from Guan et al. [34] included for comparison. The inset is the calibration curve of the syringe method for viscosity measurement using glycerol-water mixtures (the circles are the experimental data, and the line is the linear regression).

The bitumen-coated sand was packed wet in a KontesTM ChromaflexTM column (Kimble Chase, Rockwood, TN, USA) of 2.5 cm diameter and 15 cm height. The column was packed by first adding some packing solution, followed by the bitumen-coated sand in 0.5 cm increments in packed bed height. The oil sand was gently tapped with a glass rod to ensure a homogeneous packing. A 0.4% sodium dodecyl sulfate (SDS) solution was used as packing fluid to reduce the surface tension and mitigate air bubble entrainment during the packing process. It is important to note that no bitumen was detached during the packing process (no bitumen clumps or oily sheen on the surface of the packing solution). The total volume of packing fluid that was utilized and the mass of oil sand packed were recorded once the column was fully packed. The porosity of the packed column (ϵ_0) was calculated as $\epsilon_0 = (\text{volume of packing fluid} + \text{volume of bitumen associated with the packed sand}) / (\text{volume of the column, which was } 73.63 \text{ mL})$. The initial bitumen saturation (S_{n0}) was calculated as $S_{n0} = (\text{volume of bitumen associated with the packed sand}) / (\text{volume of packing fluid} + \text{volume of bitumen associated with the packed sand})$.

The packed column was connected to the experimental setup, as shown in Figure 5. A Cole-Parmer Masterflex[®] L/S[®] digital peristaltic pump drive (model 7523-60) equipped with a Masterflex[®] Easy-Load[®] pump head (model 7518-10) (Cole-Parmer, Montreal, QC, Canada) was used to control the flow rate. The tubing used was Masterflex[®] Tygon[®] (R-3603) L/S[®] 13

(Cole-Parmer, Montreal, QC, Canada). The effluents from each test were collected with a RediFrac-100 fraction collector (Amersham Biosciences, Uppsala, Sweden) at time intervals adjusted to obtain 3 mL fractions.

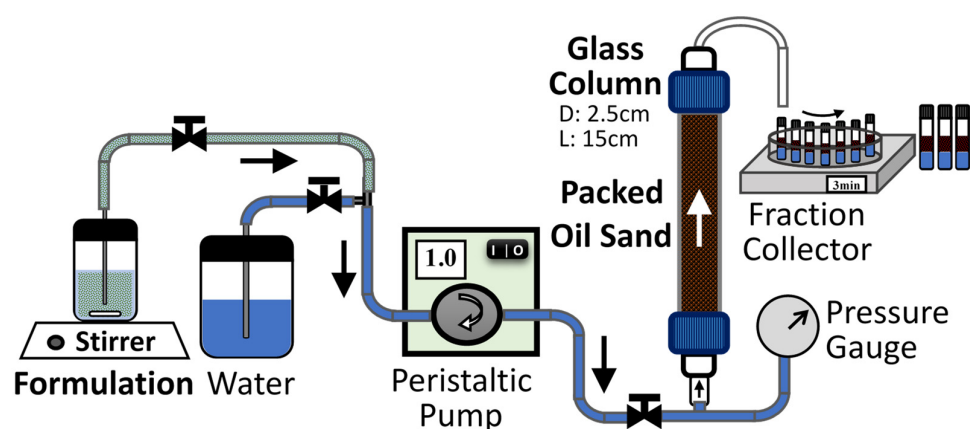


Figure 5. Experimental setup for column flooding experiments.

3.5. Permeability Measurement

The initial Darcy permeability of the column (k_{D0}) was measured by flushing DiDW in upward flow, varying the flow rate in the 0.5 to 5.0 mL/min range, corresponding to a maximum Reynolds number (based on pore throat diameter) below 0.1 in all cases. The desired water flow rate was set, and the column pressure drop was allowed to reach steady state (12–15 min, characterized by pressure fluctuations of less than 1 inch of water over a 5-min interval) before recording. No bitumen was recovered during any of the initial permeability measurements. This confirmed that the SDS packing solution did not contribute to the oil recovery. The permeability (k_{D0}) was calculated by linear fitting of Darcy's law to the pressure drop vs. the volumetric flow data.

3.6. Column Flooding Experiments

The column flooding tests were conducted in three stages at a given Darcy (or superficial) velocity ($v_D = \text{flow rate}/\text{cross-sectional area of the column}$). First, water (~ 1 PV) was flushed upwards. Next, the desired SOW formulation volume was injected, followed by ~ 0.5 PV of chase water, consistent with similar injection schemes used by others [9,10]. The SOW formulation was injected at a given salinity and water-to-solvent (W/SI) ratio. The tests were designed to deliver a total amount of solvent to reach a theoretical dilution ratio of $SI/B = 2.0$. This ratio was chosen to ensure a significant viscosity reduction of the bitumen to facilitate its detachment and displacement through the column, and it is comparable to other studies [9,10,33]. As per Figure 4, $SI/B = 2$ produces a viscosity of ~ 5 mPa·s, leading to a viscosity ratio $\mu_{DB}/\mu_c \sim 5$, which is the maximum viscosity ratio where a viscous oil can be emulsified by a shear flow [35]. Two additional control experiments were conducted, one with an aqueous surfactant formulation without emulsified cyclohexane and another, the injection of pure cyclohexane without the surfactant solution.

3.7. Oil Recovery Determination

To determine the bitumen content in each of the collected effluent vials, a spectrophotometry technique was adopted due to its acceptable accuracy and scalability to process numerous samples [9,35] compared to chromatography techniques that, while more accurate and detailed, are more resource-intensive [36]. An absorbance (optical density) calibration curve (400 nm wavelength) was developed at different toluene/bitumen dilution ratios using a Pharmacia LKB-Ultrospec Plus spectrophotometer model 80-2092-26

(Pharmacia, Cambridge, UK). Toluene was chosen as the solvent because it completely dissolves asphaltenes. First, the collected effluent vials were centrifuged at 3000 rpm for 5 min to break any stable emulsions (rag layers). Next, the volumes of the collected oil and aqueous phases in each effluent vial were estimated by measuring the height of each phase. Then, toluene (5 mL) was added to each effluent vial and tumbled. Next, the vials were centrifuged at 3000 rpm for 5 min. An aliquot of 100 μL was subsampled from the supernatant and mixed with an additional 5 mL of toluene. This 2-step dilution was required to ensure that the samples were within the detection range of the spectrophotometer. The absorbance was measured from this diluted subsample, and the original bitumen content was determined via mass balance. Similarly, to measure the residual bitumen content in the column, the sand was mixed with 300 mL of toluene. A 100 μL sample of the toluene-residual bitumen solution was mixed with an additional 5 mL of toluene as described above. The residual bitumen collected during the final permeability measurement was mixed with 150 mL of toluene, subsampled and diluted again as previously described. The final oil recovery was calculated via mass balance. At every step, samples were wrapped in Parafilm[®] (Amcor, Neenah, WI, USA) to minimize evaporation losses.

4. Results and Discussions

4.1. HLD-NAC Phase Behavior and Interfacial Tension (IFT) Prediction

Figure 6A presents pictures of test tubes produced with the AOT/Sole ($C_{\text{Total}} = 0.83\%$)-cyclohexane-diluted bitumen ($\text{SI/B} = 2$)-water for a systems at the inversion point ($S^* = 1\%$ NaCl), below the inversion point (0.5% NaCl), and above the inversion point (1.5% and 2.0% NaCl), along with the equilibrium IFT measured for those systems (points), and the equilibrium IFT values predicted by the HLD-NAC model of Figure 1, calculated using the inputs of Table 1.

The bottom (aqueous) phase obtained at 0.5% NaCl has a brown-yellow tinge, consistent with the expected micellar solubilization of oil components in the aqueous phase, while the bottom phases for 1.5 and 2% NaCl are clear, compatible with the HLD-NAC prediction that at those salinities the surfactant is primarily located in the oil phase, forming reverse micelles. At 1% NaCl, the predicted HLD is -0.01 , suggesting that this salinity is, for practical purposes, the inversion point. Although no middle phase microemulsion is observed at this point, this was expected because the total surfactant concentration ($C_{\text{Total}} = 0.83\%$) was just enough to produce ultralow IFTs as per Stammitti [23]. This is the critical microemulsion concentration ($C_{\mu\text{C}}$), distinct from CMC, which is the minimum surfactant concentration required to attain ultralow IFT, as shown in the Supplementary File. It is also worth mentioning the presence of a black precipitate that is visible at the bottom of the tube with 1.5% NaCl. This precipitate has also been observed in other studies in systems near the phase inversion point of diluted bitumen microemulsions, and has been associated with partial asphaltene rejection from microemulsion environments [14].

The HLD-NAC predicted IFT (solid line in Figure 6A) overpredicts the IFT of systems with 0.2 – 0.5% NaCl but underpredicts the IFTs at all other salinities; however, the lowest measured ultralow IFT at 1% NaCl is consistent with the lowest IFT predicted by the HLD-NAC model. Overall, there is a consistent trend between the HLD-NAC predicted IFT changes and the measured ones, which is significant considering that there were no fitted or adjusted parameters.

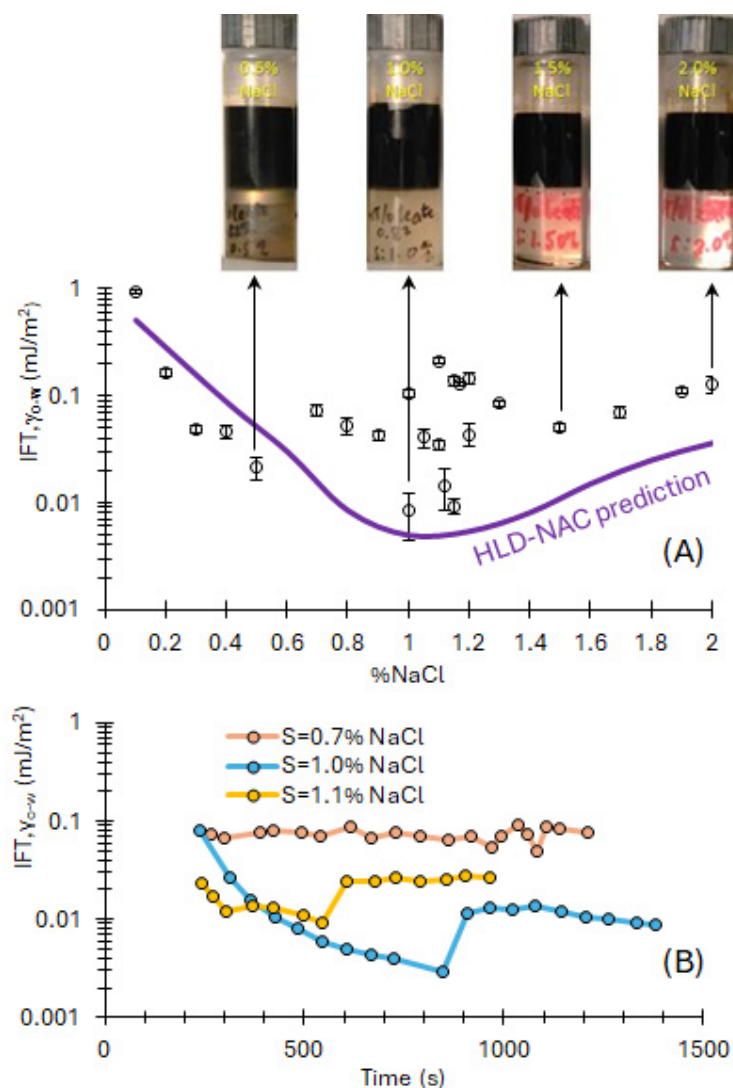


Figure 6. (A) Phase behavior and equilibrium interfacial tension (IFT) at 25 °C as a function of sodium chloride concentration (S , % NaCl) for the AOT/SOLE ($C_{\text{Total}} = 0.83\%$)-cyclohexane-diluted bitumen ($SI/B = 2$)-water system (circles) and the IFT predicted via the HLD-NAC model (solid line) using the HLD-NAC algorithm of Figure 1 and the input data of Table 1. The error bars correspond to the standard deviations of a given measurement. (B) Dynamic IFT curves for selected salinities near the phase inversion point.

Although the standard deviation of the measurements (internal replicates) in Figure 6A (the error bars) was relatively small, measurements of repeated test tubes (external replicates) varied substantially, particularly in the 1–1.2% NaCl range. To investigate this further, Figure 6B presents the dynamic IFT measurements of systems containing 0.7, 1, and 1.1% NaCl. While the system at 0.7% NaCl produced a nearly constant IFT ~ 0.07 mJ/m², the IFTs at 1 and 1.1% NaCl displayed a minimum value (closer to the value predicted by the HLD-NAC) followed by a sudden increase in IFT. It has been proposed that, around HLD ~ 0 for diluted bitumen, the HLD-NAC predicted IFT is lower than the measured IFT because of surfactant losses to the oil due to the binding of anionic surfactants to alkaline groups (e.g., pyridines) in the asphaltenes and resins in bitumen [15]. Nevertheless, given that the dynamic trends support the accuracy of the HLD-NAC predictions, these HLD-NAC predicted values will be taken as the IFT (γ_{o-w}) used to calculate the capillary numbers for the implementation of the CSTR model.

4.2. CSTR Model Fit of Bitumen Recovery and the Prediction of Viscosity and Pressure Drop

Figure 7A,D,G, and J present the CSTR-fitted (red lines) oil recovery curves for columns 1 through 4, respectively. The emulsion formulations, input parameters for the CSTR model, and the values of the unavailable bitumen saturation (S_{nU}) and the critical particle-based Capillary number ($Ca_{p,crit}$), resulting from the CSTR model fit for each column, are listed in Table 2. The $\pm$ values for S_{nU} and $Ca_{p,crit}$ represent the 95% confidence interval, obtained from the excursion (perturbation) method [37]. Overall, the CSTR model can reproduce the experimental oil recoveries reasonably well. The largest deviation was observed with column #3 (C#3), and the reason is that this column, for logistical reasons, had to be stopped overnight to then resume the emulsion injection the next day. The overnight flow stop did not prevent other processes from occurring, particularly diffusion of the solvent into bitumen and buoyancy-driven movement of diluted bitumen towards the top of the column. The next day, the diluted bitumen that had moved towards the top of the column produced a large increase in the production rate of bitumen. The CSTR fit for C#3 was conducted as if it were a single continuous extraction, but clearly it should have been treated as two separate events. The other case in which the CSTR model did not reproduce the full experimental curve was solvent-only injection in C#4. In that case, the last stage of water flush produced a small but noticeable increase in bitumen recovery. None of the CSTR fits included the last step of water flush.

Table 2. Input and fitted parameters of the CSTR model.

Parameter	C#1	C#2	C#3	C#4
Emulsion formulation				
S, % NaCl	0.75	1.1	0.83	Solvent only
W/SI (v/v ratio)	3	3	10	0
Input parameters for the CSTR algorithm				
S_{n0}	0.455	0.50	0.467	0.477
v_D , m/d	2.05	2.05	2.05	2.05
ε_o	0.411	0.377	0.402	0.394
γ_{o-w} , mJ/m ²	0.011	0.005	0.008	29
k_{Do} , Darcy	1.46 ± 0.04	0.96 ± 0.04	1.22 ± 0.01	0.9 ± 0.2
f_λ	1000	1000	1000	1000
L_c , m	0.15	0.15	0.15	0.15
τ_p/τ_d	22.0	22.7	65.6	30.7
Fitted parameters of the CSTR algorithm				
S_{nU}	0.07 ± 0.04	0.21 ± 0.02	0 ± 0.06	0.3 ± 0.02
$Ca_{p,crit}$	0.012 ± 0.002	0.02 ± 0.002	0.012 ± 0.003	$(7 \pm 2) \times 10^{-6}$
Oil (bitumen + solvent) saturation before final water flush				
$S_{nf} = S_{nU} + S_{nDB@end}$	0.76	0.69	0.68	0.88
$S_{nf_assessed}$	0.67	0.59	0.38	0.97

Figure 7B,E,H,K present the measured oil viscosities (data points), and the CSTR-predicted produced oil viscosities (red lines). For columns C#1, C#2, and C#4, the CSTR-predicted viscosities are consistent with measured values. For C#3, the overnight stop created swings in viscosity that could not be reflected by the CSTR prediction.

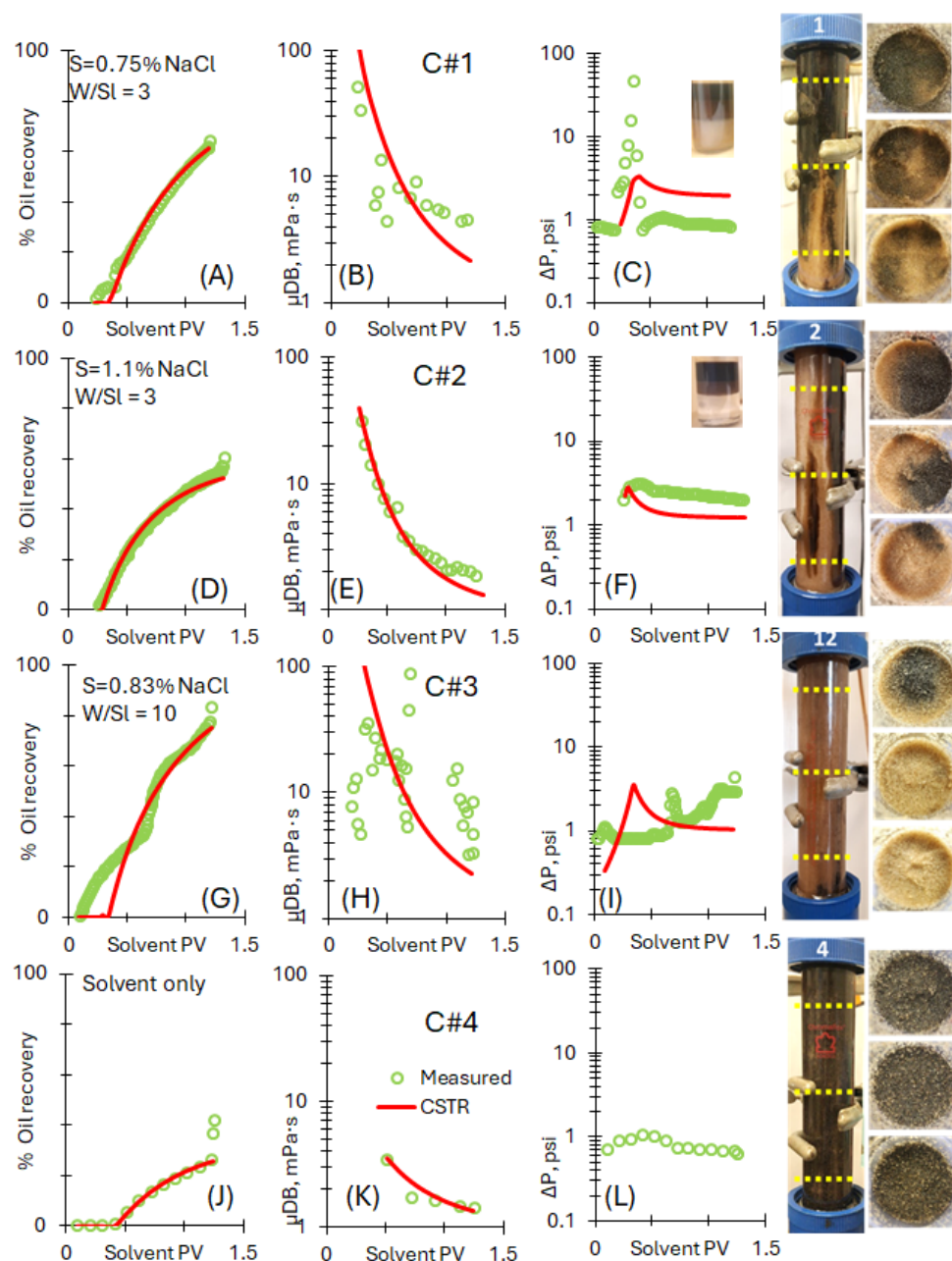


Figure 7. (A,D,G,J) Oil recovery curves (% bitumen recovery vs. injected solvent pore volume), (B,E,H,K) Produced oil viscosity curves (viscosity of the oil effluent vs. solvent pore volume), (C,F,I,L) Pressure drop curves (pressure drop across the packed column vs. solvent pore volume). The first row of data corresponds to column #1 (C#1) obtained after injecting an emulsion with a salinity (S) of 0.75% NaCl and a water/solvent volume ratio (W/SI) of 3. The second row, C#2, was obtained with $S = 1.1\%$ and $W/SI = 3$. The third row, C#3, was obtained with $S = 0.83\%$ and $W/SI = 10$. The fourth row, C#4, was obtained by injecting only solvent. Columns 1 through 3 contain $C_{\text{total}} = 0.83\%$ of the AOT/Sole mixture. The pictures at the end of each row show the column after the final water flush. The red lines represent the fits (A,D,G,J) and predictions (all others) from the CSTR algorithm. The yellow dotted lines represent the location of the column's cross-sections.

Figure 7C,F,I,L present the measured pressure drop (data points) and the CSTR-predicted pressure drops (red lines). For C#1, C#2 and C#3, the CSTR predicts a peak in pressure drop at the moment the production stage starts, which is due to an increase in diluted bitumen saturation (S_{DB}) to the maximum level possible (S_{max}), which produces a maximum level of restriction of the flow of water through the porous media. The S_{max} at

that early production stage is the largest Sn_{max} throughout the emulsion injection because at that point the viscosity of the diluted bitumen is the largest, producing the lowest $Ca_{p,crit}$, as per Equation [B14]. For C#1, it is not clear why the measured pressure drop, after reaching peak pressure drop, reduces to nearly half the predicted pressure drop, particularly when considering the underprediction after peak pressure drop for C#2. For the case of C#3, the continuous CSTR fit does not match the experimental trends; however, one could note that the measured pressure drop has one peak at ~ 0.07 SIPV and ~ 0.65 SIPV, corresponding to the two-step increase in oil production resulting from the overnight stop. For C#4, the CSTR model was not used to predict pressure drop because it was not a 2-phase flow throughout the entire solvent flushing step.

The pictures of columns C#1 through C#4 on the right side of their corresponding rows in Figure 7 illustrate the state of the columns after the final water flush. Overall, the cross-section images match the oil-removal levels for each column. However, the pictures also illustrate, particularly for columns C#1 and C#2, the prevalence of preferential flow paths, as expected due to the low viscosity of the injected emulsion and the high viscosity of the diluted bitumen, particularly in the early production stages. This preferential flow path behavior suggests that the pore-scale view in Figure 2 of “available” and “unavailable” bitumen might not be accurate at the pore scale, but rather it is realized by areas of the column that are “unavailable” for dilution with the solvent because the solvent is carried through the preferential flow paths. The lack of bitumen streaks in C#3 (i.e., no evidence of prevalent preferential flow paths) suggests that the combination of slow solvent addition (use of $W/SI = 10$) and one or more stop-flow events helps minimize the risk of preferential flow and increase the overall bitumen extraction. Although the pore-scale view in Figure 2 is not entirely accurate, the concept of “available” and “unavailable” bitumen fractions is appropriate for capturing these preferential flow effects at a macroscopic scale using the CSTR model.

The inset pictures in Figure 7C,F show the vials of produced emulsion collected towards the end of the production stage. The objective of these pictures is to illustrate the level of oil-water separation that can be obtained with each formulation (the vials were not centrifuged, and pictures were taken within 15 min after collection). For the vial in Figure 7C, prepared at a negative HLD ($HLD = -0.35$ at $S = 0.75\%$ NaCl), the aqueous (bottom) phase shows signs of a partially stable oil-in-water emulsion, which is consistent with this HLD. For the vial of Figure 7F, prepared with near-zero HLD ($HLD = +0.03$ at $S = 1.1\%$ NaCl), the aqueous phase is clear, and even the rag layer (brownish layer separating the water from the top oil phase) is smaller compared to the rag layer in Figure 7C. This observation is consistent with the fact that at $HLD \sim 0$, one expects fast demulsification, a desirable feature for downstream separation of the produced oil.

Table 2 summarizes the oil (bitumen + solvent) saturation levels at the end of the emulsion injection period (Sn_f), obtained from the CSTR model ($Sn_U + Sn_{DB}$) and the value assessed from the experimentally determined bitumen recovery (%rec) and from the solvent/bitumen (SI/B) ratio estimated from the viscosity of the produced diluted bitumen, $Sn_{f,assessed} = Sn_0 \cdot (1 - \%rec)(1 + SI/B)$. With the exception of C#3, the CSTR-predicted residual saturations are within ± 0.1 volume fraction of the values assessed from experimental measurements. For C#3, the relatively low $Sn_{f,assessed}$ is likely linked to the inaccuracy of the continuous CSTR approach to reflect the two-step behavior produced by the overnight stop. Nevertheless, the most important point is that, except for C#3, $Sn_f > Sn_0$. In other words, it would appear that, for C#1 and C#2, the ultralow IFT did not produce the expected decrease in oil saturation, as it has been observed for the case of conventional surfactant-enhanced oil recovery (S-EOR). However, one must remember that the solvent (cyclohexane) was co-injected with the surfactant solution; thus, any removal

of oil (solvent + bitumen mixture) was accompanied by the deposition of the solvent on the porous media. To realize lower Sn_f , the emulsion injection should have been followed by a surfactant-only injection to recover the deposited solvent. Unfortunately, we did not consider this post-emulsion surfactant flooding step, resorting to water-only post-emulsion injection, following previous protocols.

This study represents the first time that a particle-based capillary number ($Ca_{p,crit}$), developed to understand oil removal from falling oil-coated spheres [25,35], is extrapolated to understand oil removal from porous media. In oil-coated spheres, the maximum oil removal was obtained when $Ca_p \sim 0.1$ to 1, because in that range one obtained the largest effect of shear to deform the oil-water interface and the minimum interfacial tension resistance to deformation. There is no guarantee that the same Ca_p range applies to porous media, but if so, it suggests that the $Ca_{p,crit}$ are still too low to guarantee complete oil removal. Stammitti conducted column studies for the conditions of C#2 at $v_D = 9.1$ m/d and $W/SI = 10$, reaching $Ca_{p,crit} \sim 0.1$ where the largest oil recovery was obtained (~60% oil recovery) when injecting only 0.5 PV of solvent [23]. This large early oil recovery, however, was accompanied by a large increase in pressure drop. This observation suggests that $Ca_{p,crit} \sim 0.1$ –1 might reach optimal oil recovery, even in porous media.

4.3. CSTR Model Prediction of Bitumen Recovery and Pressure Drop

The previous section showed that for various surfactant formulations, $Ca_{p,crit}$ ranges from 0.01 to 0.02, which is a relatively narrow range that allows making an educated guess to predict the removal of oil for other extraction conditions. On the other hand, the unavailable saturation (Sn_U) showed ample variability that needs to be correlated with other process variables to make reasonable predictions for other extraction conditions.

One potential interpretation of Sn_U is that high values might result from insufficient time for the solvent to penetrate and dissolve the bitumen film. To assess this possibility, a ratio of pore residence time scale (τ_p) to diffusion time scale (τ_d) was calculated. The pore residence time scale was estimated as $\tau_p \sim (1 + W/SI)(\text{sand grain size})/(v_D/(\epsilon_o \cdot Sn_0))$. The term $(1 + W/SI)$ reflects the fact that depositing a given volume of solvent in the pore takes more time when the water-to-solvent ratio is higher, given that the injected emulsion flowrate is fixed (to give the set Darcy velocity, v_D). The term $v_D/(\epsilon_o \cdot Sn_0)$ transforms the Darcy velocity into the pore velocity of the fed emulsion traveling through the bitumen-coated pore. For the grain size, an average grain size of 250 μm was assumed in the calculations.

To calculate the diffusion time scale, the first step is to assess the initial (undiluted) bitumen film thickness as $d_{th0} = (1 - (1 - Sn_0)^{0.5}) \cdot [8k_{D0}/(\epsilon_o \cdot (1 - Sn_0))]^{0.5}$. This equation was obtained considering a porous medium as a bundle of pipes [38], that the ratio between the porosities of the bitumen-coated porous media and the bitumen-free porous media is $(1 - Sn_0)$, and that this ratio represents the ratio of the cross-sectional areas of the bitumen-coated and the bitumen-free porous media. The diffusion time scale is then estimated as $\tau_d \sim (d_{th0})^2/D_{Sl}$, where D_{Sl} is the diffusivity of the solvent in undiluted bitumen, taken as $D_{Sl} \sim 10^{-11}$ m^2/s , a value that reflects the order of magnitude of the toluene (similar in size to cyclohexane) diffusivity in bitumen [39]. Table 2 presents a summary of these τ_p/τ_d ratios, and Figure 8A plots Sn_U vs. τ_p/τ_d for the column studies in Table 2. Overall, the trendline in Figure 8A shows the expected trend of reducing Sn_U with increasing τ_p/τ_d , but the correlation is too poor ($R^2 \sim 0.35$) to use it as a predictive tool.

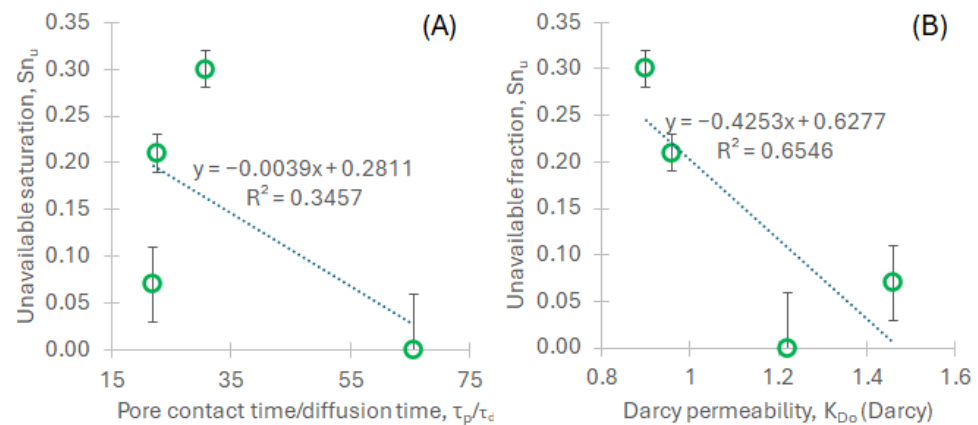


Figure 8. Correlation between unavailable bitumen saturation (S_{n_u}) for column C#1 through C#4 with pore contact time/diffusion time (τ_p/τ_d) (A) and with the column permeability (k_{Do}) (B). The error bars represent the 95% confidence interval for the fitted S_{n_u} values. The dotted lines represent the regression lines.

Another interpretation for high S_{n_u} is that there are regions in the column where the emulsified solvent has poor access to bitumen. Figure 8B shows a significant ($R^2 \sim 0.65$) trend of reducing S_{n_u} with increasing permeability (k_{Do}), supporting the poor access hypothesis. This interpretation is consistent with the streaks of bitumen-containing sand seen in the pictures of columns C#1 and C#2 in Figure 7. The correlation in Figure 8B is high enough to use it as a predictive tool.

To assess the ability of the CSTR model to predict the outcome of other TESI conditions, the performance of column studies conducted with increased Darcy velocity ($v_D = 4.4$ m/day), $S = 1.1\%$ NaCl (0.83% AOT/Sole solution), and at W/SI ratios of 3 (Column #5), 5 (Column #6), and 10 (Column #7) was predicted using the input listed in Table 3. The value of $Ca_{p,crit} = 0.02$, used in all columns in Table 3, was extrapolated from the condition in Column #2, which also used $S = 1.1\%$ NaCl. The value of S_{n_u} for each column in Table 3 was estimated based on the permeability measured for each column (k_{Do}), and the regression line of Figure 8B.

Table 3. Input and predicted parameters of the CSTR model.

Parameter	C#5	C#6	C#7
S, % NaCl	1.1	1.1	1.1
W/SI (v/v ratio)	3	5	10
Input parameters for the CSTR algorithm			
S_{n_0}	0.446	0.461	0.471
v_D , m/d	4.4	4.4	4.4
ε_o	0.4	0.397	0.382
γ_{o-w} , mJ/m ²	0.005	0.005	0.005
k_{Do} , Darcy	1.02 ± 0.04	0.92 ± 0.04	1.11 ± 0.03
f_λ	1000	1000	1000
L_c , m	0.15	0.15	0.15
τ_p/τ_d	14.6	22.2	29.7
Predicted parameters for the CSTR algorithm			
S_{n_u}	0.19	0.24	0.16
$Ca_{p,crit}$	0.02	0.02	0.02
Oil (bitumen + solvent) saturation before final water flush			
$S_{n_f} = S_{n_u} + S_{n_{DB@end}}$	0.48	0.51	0.45

Figure 9 presents the experimental (data points) and CSTR-predicted (red line) oil recovery (Figure 9A,C, and E) and pressure drops (Figure 9B,D, and F) for columns C#5, C#6 and C#7 (first, second and third row of graphs, respectively). Overall, the CSTR prediction was reasonable as a potential screening tool, predicting the final recovery within $\pm 10\%$, and the initial breakthrough of oil recovery within ± 0.1 solvent PV. For higher W/SI ratios, the final recovery tends to be underpredicted, likely because the weak trend between Sn_U and τ_p/τ_d (Figure 8A), which is highly influenced by W/SI was ignored. The pressure drop predictions for Columns C#5 and C#6 show the initial pressure drop peak observed in the experiments, but the pressure drop after 0.5 solvent pore volumes is consistently underpredicted by a factor of 2 to 4 in all the columns. One possible explanation for this mismatch is that the CSTR model assumes that the geometry of the pores is constant throughout the experiment, but as the bitumen is removed, the packed sand could reconfigure (at least in some sections of the column) to produce a tighter packing that would explain the higher pressure drop. It is relevant to clarify that although the CSTR model predicted the viscosity of the produced diluted bitumen for C#5, C#6, and C#7, these predictions were not included in Figure 9 because the corresponding experimental values were not measured.

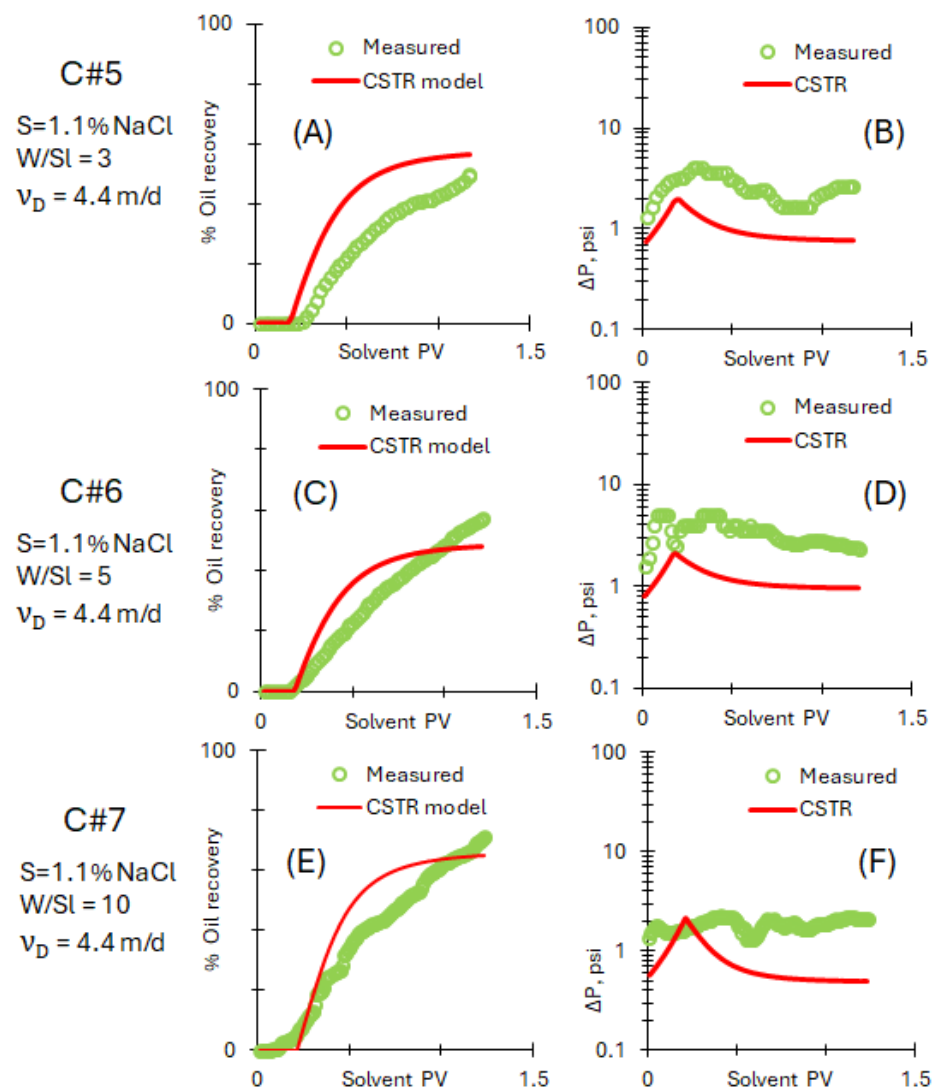


Figure 9. (A,C,E) Oil recovery curves (% bitumen recovery vs. injected solvent pore volume). (B,D,F) Pressure drop curves (pressure drop across the packed column vs. solvent pore volume). The

first row of data corresponds to column #5 (C#5) obtained at a water/solvent volume ratio (W/SI) of 3. The second row, C#6, was obtained with W/SI = 5. The third row, C#7, was obtained with W/SI = 10. All the column studies were conducted using $C_{\text{Stotal}} = 0.83\%$ of the AOT/Sole mixture, and $S = 1.1\%$. The red lines represent the predictions obtained with the CSTR algorithm, and the input data of Table 3.

5. Conclusions

This work explored the use of targeted-emulsified solvent injection (TESI) technology for the removal of bitumen from packed columns of simulated oil sands, comparing modeling approaches to experimental data obtained by Stammitti [23]. The interfacial tension of a surfactant mixture of sodium oleate (Sole) and dioctyl sulfosuccinate (Aerosol OT or AOT) with bitumen diluted with cyclohexane was predicted using the HLD-NAC model, considering the polar oil behavior of naphthenic acids that are naturally occurring in bitumen. The model led to reasonable predictions of IFT, but also confirmed partition issues that have previously been reported to prevent stable ultralow IFTs in bitumen systems. The oil recovery experiments were modeled using a CSTR model that considered pore-scale deposition of solvent and release of diluted bitumen, including a provision for a fraction of unavailable bitumen that does not mix with the solvent. Overall, the CSTR model was able to fit the bitumen recovery curves and even predict the viscosity of the produced diluted bitumen and the trends in pressure drop curves. The largest deviation from the CSTR model was obtained with an experiment that was stopped overnight, where it is hypothesized that buoyancy effects played a role in increasing the oil production once the injection of the emulsified solvent resumed. This particular study produced the largest oil recovery in all the studies reported by Stammitti.

Through the evaluation of cross-sections of the column after completion, it was determined that the unavailable fraction in the CSTR model represented the portion of the bitumen that the injected emulsion did not sweep due to preferential flow paths (viscous fingering). The particle-based capillary number ($Ca_{p,crit}$), extrapolated from the definition of oil-coated spheres, seems to point to values of 0.1–1 to maximize the oil extraction with minimum solvent addition, a condition that is consistent with the optimal values for oil removal in the original definition.

The conditions considered in this work are far from optimal, but they all give clues to optimize the bitumen and solvent recovery using TESI. These conditions include: (i) using larger W/SI ratios, for example, 10/1; (ii) introducing various stop-flow intervals to take advantage of buoyancy forces; (iii) introducing a surfactant-only flooding after emulsion injection to recover most of the solvent left in the porous media; (iv) increase $Ca_{p,crit}$ to 0.1–1, partially by promoting ultralow IFT, partially by increase the superficial velocity of the aqueous phase, but also by increasing the viscosity of the aqueous phase, which should reduce the viscosity ratio and the chances for viscous fingering.

Although the costs of the technology were not discussed, compared to steam injection, the capital costs are substantially reduced because the water injected does not have to be of high quality and could be recovered using simple gravity settlers. Most of the surfactant is expected to remain in the aqueous phase; thus, only a make-up quantity is required before water reinjection. The main cost driver of the process is the amount of solvent left in the reservoir; thus, the need to maximize the recovery of the solvent by implementing a combination of the strategies mentioned in the previous paragraph. From a sustainability point of view, compared to steam injection, TESI does not have large energy requirements since the heat for solvent recovery would be similar to the current solvent recovery in bitumen upgrading, and no steam production is required. Furthermore, there is a possibility

of introducing solvents that can induce partial precipitation of asphaltenes in the reservoir, reducing the upgrading needs (preliminary data, suggest the viability of this approach).

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/colloids10040053/s1>, This section includes the development of the mass balance equation for the CSTR model illustrated in Figure S1. Figure S1. CSTR volume (V_{DB}), solvent flow (V_{flow}) and bitumen concentration (C_B). The supplementary material also includes references associated with the concept of critical microemulsion concentration ($C_{\mu C}$) [40–42], and the interfacial tension data used to identify it in this work is included in Figure S2. Figure S2. Interfacial tension vs. total surfactant concentration for the AOT/SOLE-CHX/B (S/B = 2.0)-water system at S = 1.1%.

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Data Availability Statement: The original experimental data can be found in the open-source thesis dissertation of Aurelio Stammitti at: Solid–liquid–liquid Wettability and its role on Targeted Emulsified Solvent Injection (TESI). For modeling resources, the corresponding author, Edgar Acosta, can be contacted for additional information.

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References

1. Zhao, D.W.; Wang, J.; Gates, I.D. Thermal recovery strategies for thin heavy oil reservoirs. *Fuel* **2014**, *117*, 431–441. [CrossRef]
2. Ahmadi, M. *Sustainable In-Situ Heavy Oil and Bitumen Recovery: Techniques, Case Studies, and Environmental Considerations*; Elsevier: Amsterdam, The Netherlands, 2023.
3. McAuliffe, C.D. Oil-in-Water Emulsions and Their Flow Properties in Porous Media. *J. Pet. Technol.* **1973**, *25*, 727–733. [CrossRef]
4. Guillen, V.R.; Carvalho, M.S.; Alvarado, V. Pore Scale and Macroscopic Displacement Mechanisms in Emulsion Flooding. *Transp. Porous Media* **2012**, *94*, 197–206. [CrossRef]
5. Mandal, A.; Samanta, A.; Bera, A.; Ojha, K. Characterization of oil-water emulsion and its use in enhanced oil recovery. *Ind. Eng. Chem. Res.* **2010**, *49*, 12756–12761. [CrossRef]
6. Harwell, J.H.; Sabatini, D.A.; Shiau, B.J. Design aspects and practices of surfactant formulations used in chemical EOR and surfactant-enhanced aquifer remediation. In *Surfactant Formulation Engineering Using HLD and NAC*; Academic Press: Cambridge, MA, USA, 2025; pp. 99–123.
7. Chowdhury, S.; Shrivastava, S.; Kakati, A.; Sangwai, J.S. Comprehensive Review on the Role of Surfactants in the Chemical Enhanced Oil Recovery Process. *Ind. Eng. Chem. Res.* **2022**, *61*, 21–64. [CrossRef]
8. Salager, J.L.; Forgiarini, A.M.; Bullón, J. How to attain ultralow interfacial tension and three-phase behavior with surfactant formulation for enhanced oil recovery: A review. Part 1. Optimum formulation for simple surfactant-oil-water ternary systems. *J. Surfactants Deterg.* **2013**, *16*, 449–472. [CrossRef]
9. Sarbar, M.; Brochu, C.; Boisvert, M.; Desnoyers, J.E. Tar sand extractions with microemulsions and emulsions. *Can. J. Chem. Eng.* **1984**, *62*, 267–277. [CrossRef]
10. Sarma, H.K.; Maini, B.B.; Jha, K. Evaluation of emulsified solvent flooding for heavy oil recovery. *J. Can. Pet. Technol.* **1998**, *37*, 55–62. [CrossRef] [PubMed]
11. Mohammadzadeh, O.; Chatzis, I.; Giesy, J.P. A novel chemical additive for in-situ recovery of heavy oil using waterflooding process. *J. Pet. Sci. Eng.* **2015**, *135*, 484–497. [CrossRef]
12. Acosta, E.J.; Harwell, J.H. Net-Average Curvature (NAC) fundamentals. In *Surfactant Formulation Engineering Using HLD and NAC, First*; Acosta, E.J., Harwell, J.H., Sabatini, D.A., Eds.; Academic Press: Cambridge, MA, USA, 2025; pp. 259–325.

13. Johns, R.T.; Magzymov, D. Microemulsion flash calculations using an HLD-NAC-based equation of state. In *Surfactant Formulation Engineering Using HLD and NAC*; Academic Press: Cambridge, MA, USA, 2025; pp. 391–410.
14. Ghayour, A.; Perez, R.; Bhattacharya, S.; Acosta, E.J. Characterizing the Behavior of Bitumen-Water Systems with the Hydrophilic-Lipophilic Difference (HLD) framework. *Energy Fuels* **2022**, *36*, 14030–14041. [[CrossRef](#)]
15. Perez-Franco, R.; Acosta, E. Zipper-Like Linker Self-Assembly to Obtain Low Interfacial Tensions with Partially Neutralized Naphthenic Acids. *Energy Fuels* **2024**, *38*, 1729–1743. [[CrossRef](#)]
16. Tan, J.-X.; Acosta, E. Bifunctional HLD–NAC for Clove Oil Microemulsions. *Liquids* **2025**, *5*, 23. [[CrossRef](#)]
17. Acosta, E.; Perez-Franco, R.; Leng, Z.; Cordeiro, B.; Tan, J.X.; Boza-Troncoso, A.; Hammond, C.; Zarate-Muñoz, S.; Harwell, J.H. The hydrophobicity of surfactants and surfactant-oil-water (SOW) systems. In *Surfactant Formulation Engineering Using HLD and NAC, First*; Acosta, E.J., Harwell, J.H., Sabatini, D.A., Eds.; Academic Press: Cambridge, MA, USA, 2025; pp. 1–48.
18. Acosta, E.J.; Ghayour, A.; Boza-Troncoso, A.; Hill, R.; Harwell, J.H. Effect of oils and additives on the hydrophilic-lipophilic difference (HLD). In *Surfactant Formulation Engineering Using HLD and NAC, First*; Acosta, E.J., Harwell, J.H., Sabatini, D.A., Eds.; Academic Press: Cambridge, MA, USA, 2025; pp. 49–98.
19. Ghayour, A.; Acosta, E. Characterizing the Oil-like and Surfactant-like Behavior of Polar Oils. *Langmuir* **2019**, *35*, 15038–15050. [[CrossRef](#)] [[PubMed](#)]
20. Kiran, S.K.; Acosta, E.J.; Moran, K. Evaluating the hydrophilic-lipophilic nature of asphaltenic oils and naphthenic amphiphiles using microemulsion models. *J. Colloid Interface Sci.* **2009**, *336*, 304–313. [[CrossRef](#)] [[PubMed](#)]
21. Graciaa, A.; Lachaise, J.; Cucuphat, C.; Bourrel, M.; Salager, J.L. Improving Solubilization in Microemulsions with Additives. 1. The Lipophilic Linker Role. *Langmuir* **1993**, *9*, 669–672. [[CrossRef](#)]
22. Acosta, E.J. *Modeling and Formulation of Microemulsions: The Net-Average Curvature Model and the Combined Linker Effect*; University of Oklahoma: Norman, OK, USA, 2004.
23. Stammitti Scarpone, A. Solid-Liquid-Liquid Wettability and Its Role on Targeted Emulsified Solvent Injection (TESI). Ph.D. Dissertation, University of Toronto, Toronto, ON, Canada, 2019.
24. Lederer, E.L. Viscosity of mixtures with and without diluents. *Proc. World Pet Cong Lond.* **1933**, *2*, 526–528.
25. Mehrabian, S.; Acosta, E.; Bussmann, M. Oil-particle separation in a falling sphere configuration: Effect of viscosity ratio & interfacial tension. *Int. J. Multiph. Flow* **2018**, *98*, 120–127. [[CrossRef](#)]
26. Berg, S.; Cense, A.W.; Hofman, J.P.; Smits, R.M.M. Two-phase flow in porous media with slip boundary condition. *Transp. Porous Media* **2008**, *74*, 275–292. [[CrossRef](#)]
27. Lemahieu, G.; Ontiveros, J.F.; Molinier, V.; Aubry, J.-M. Rheology as a tool for identifying and characterizing optimal microemulsions formulations. *J. Surfactants Deterg.* **2025**, *28*, 627–638. [[CrossRef](#)]
28. Olayiwola, S.O.; Dejam, M. Interfacial energy for solutions of nanoparticles, surfactants, and electrolytes. *AIChE J.* **2020**, *66*, e16891. [[CrossRef](#)]
29. Wang, T.; Zhang, C.; Zhao, R.; Zhu, C.; Yang, C.; Liu, C. Solvent extraction of bitumen from oil sands. *Energy Fuels* **2014**, *28*, 2297–2304. [[CrossRef](#)]
30. Pal, K.; Nogueira Branco, L.d.P.; Heintz, A.; Choi, P.; Liu, Q.; Seidl, P.R.; Gray, M.R. Performance of Solvent Mixtures for Non-aqueous Extraction of Alberta Oil Sands. *Energy Fuels* **2015**, *29*, 2261–2267. [[CrossRef](#)]
31. Zarate-Muñoz, S.; Texeira De Vasconcelos, F.; Myint-Myat, K.; Minchom, J.; Acosta, E. A Simplified Methodology to Measure the Characteristic Curvature (Cc) of Alkyl Ethoxylate Nonionic Surfactants. *J. Surfactants Deterg.* **2016**, *19*, 249–263. [[CrossRef](#)]
32. Leonard, R.C. Simple technique for measuring serum or plasma viscosity with disposable apparatus. *Br. Med. J.* **1981**, *283*, 1154–1155. [[CrossRef](#)] [[PubMed](#)]
33. Quraishi, S.; Bussmann, M.; Acosta, E. Capillary Curves for Ex-situ Washing of Oil-Coated Particles. *J. Surfactants Deterg.* **2015**, *18*, 811–823. [[CrossRef](#)]
34. Guan, J.G.; Kariznovi, M.; Nourozieh, H.; Abedi, J. Density and Viscosity for Mixtures of Athabasca Bitumen and Aromatic Solvents. *J. Chem. Eng. Data* **2013**, *58*, 611–624. [[CrossRef](#)]
35. Mehrabian, S.; Acosta, E.; Bussmann, M. Oil-Particle Separation in a Falling Sphere Configuration: Effect of Oil Film Thickness. *Energy Fuels* **2016**, *30*, 8776–8786. [[CrossRef](#)]
36. Karevan, A.; Kheirollahi, S.; Zirrahi, M.; Hassanzadeh, H. A new chromatographic approach for bitumen characterization and solvent concentration measurement. *Fuel* **2023**, *339*, 126907. [[CrossRef](#)]
37. Leng, Z.; Acosta, E. The characteristic curvature (Cc) definition and its use in assessing Cc for single ionic surfactants. *J. Surfactants Deterg.* **2023**, *26*, 287–301. [[CrossRef](#)]
38. Ma, S.; Morrow, N. Relationships between porosity and permeability for porous rocks. In *Proceedings of the International Symposium of the Society of Core Analysts*, Montpellier, France, 8–10 September 1996; pp. 8–10.
39. Fadaei, H.; Shaw, J.M.; Sinton, D. Bitumen–Toluene Mutual Diffusion Coefficients Using Microfluidics. *Energy Fuels* **2013**, *27*, 2042–2048. [[CrossRef](#)]

40. Aveyard, R.; Binks, B.P.; Clark, S.; Fletcher, P.D.I. Effects of temperature on the partitioning and adsorption of C12E5 in heptane-water mixtures. *J. Chem. Soc.—Faraday Trans.* **1990**, *86*, 3111–3115. [[CrossRef](#)]
41. Acosta, E.J.; Harwell, J.H.; Sabatini, D.A. Self-assembly in linker-modified microemulsions. *J. Colloid Interface Sci.* **2004**, *274*, 652–664. [[CrossRef](#)] [[PubMed](#)]
42. Aveyard, R.; Binks, B.P.; Mead, J.; Clint, J.H. Interfacial tensions and microemulsion formation in heptane–aqueous NaCl systems containing aerosol OT and sodium dodecyl sulphate. *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **1988**, *84*, 675–686. [[CrossRef](#)]

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