

## A COLLOIDAL MODEL FOR ASPHALTENE FLOCCULATION FROM PETROLEUM FLUIDS\*

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**Abstract** - The need to understand the nature of asphaltenes and asphalts and their role in the production, transportation and processing of crude oil is well-recognized internationally, as manifested by the current activities in the petroleum industry towards exploration, drilling, production and processing of heavier oils (higher in asphaltene content). Asphaltene deposition during oil production and processing ranks as one of the costliest technical problems the petroleum industry currently faces. In the present report, a colloidal model has been developed, capable of predicting the onset of flocculation of colloidal asphaltene in oil mixtures, due to either changes in composition (i.e., solvent addition) or electrical phenomena (i.e., streaming potential generation due to flow of asphaltenes containing oil in conduits or porous media). For oil mixtures from which flocculation is caused simply by flow, the model can make predictions as to the velocity ranges where colloidal asphaltene flocculation can be avoided. This could have a significant impact on allowed reservoir drawdown rates, well spacing and tubing design. The present model is a part of a comprehensive asphaltene FRACTAL aggregation model (ASPHRAC) being developed at the University of Illinois.

### 1. INTRODUCTION

#### *Field experience and related research:*

Asphaltene deposition is a very serious problem which has been faced by the oil industry for many years. The significance of the problem was discussed at length by the authors in an earlier paper [1]. Asphaltene or asphalt deposition around the well bore, well tubings, flowlines, separators, pumps, tanks and other equipment has, on many occasions, threatened the oil's economic recovery or considerably increased its production cost. Such cases were reported in the Prinos Field, Greece [2], the Mata-Acema Field, Venezuela [3], the Hassi-Messaoud Field, Algeria [4], the Ventura Avenue Field, California [5], and other places throughout the world.

The asphaltene problem is so insidious that, in all known cases, the difficulty was

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unforeseen during exploration or even the development phase of oil discovery. As a result, the oil producer became aware of the problem only after a very large portion of the capital expenditure was already spent, making it difficult, if not impossible, from an economic standpoint, to quit the project. Thus it is important to the producer that any potential asphaltene problems be predicted and the impact of remedial measures, if any, in the project's economics be evaluated before field development takes place. This evaluation could be a very crucial factor in the decision of whether or not to develop the field.

*Past laboratory studies:*

Substantial research both in the industrial and academic communities has been steadily taking place on the topic of asphaltene flocculation since the late 1930's [2, 3, 6-14]. At this stage, it seems that the solution of this problem calls for detailed analyses of asphaltene containing systems from the statistical mechanics and colloidal science standpoint and development of microscopic models which could describe the macroscopic behavior of asphaltenes in hydrocarbon mixtures. The available laboratory and field data indicate that the asphaltenes which exist in oil consist of very many particles which have molecular weights ranging from 1000 to several hundred thousands. As a result, distribution curves are used to report their molecular weight. The extensively wide range of asphaltene size distribution suggests that asphaltene is partly dissolved and partly in a colloidal state (in suspension), peptized (or stabilized) primarily by resin molecules that are adsorbed on the asphaltene surface. For this reason, a realistic model for the interaction of asphaltene and oil should take into account both the solubility in oil of one segment, and the suspension characteristic (due to resins) of another segment of the molecular weight distribution range of asphaltenes.

In the present report, a colloidal suspension model is presented. In developing the present model, it is assumed that asphaltenes exist in oil as small solid particles, in colloidal suspension, stabilized by resins adsorbed on their surfaces, and consist of the elements C, H, O, N, and S. Earlier research has shown that the asphaltene particles, if they exist in the original oil mixture, must have diameters less than  $65\text{\AA}$  [9]. Further work on the size distribution of asphaltene particles in the original oil has shown that the particle size is within the range of  $35\text{-}40\text{\AA}$  for the oils studied [7]. However, the available techniques and data are incapable of making a correct estimate on the size distribution of asphaltene particles in the original oil.

Other work exists which is relative to determining the size distribution of asphaltene particles, but such methods involve flocculation of the particles which, in itself, takes place after the particles have grown in size. According to these methods, asphaltene molecular weight distribution is within the range of 2,000 to 140,000 [6, 8, 15]. Future experimental work must be geared, alongside other objectives, towards shedding some light on the true size distribution of asphaltene particles and its relation to the various types of separating

solvents.

## 2. THE COLLOIDAL MODEL

The proposed model is based on statistical mechanics and colloidal science techniques and is general enough to cover the colloidal asphaltene flocculation problem, wherever it may occur, during crude oil's production and processing. The model is based on the assumption that asphaltenes exist in the oil as solid particles in colloidal suspension, stabilized by resins adsorbed on their surface. It is also assumed that the short range intermolecular repulsive forces between resin molecules adsorbed on different asphaltene particles keep them from flocculating. There would also be another weaker and longer range repulsive force present between the asphaltene particles because of their similar electrical charge. This repulsive force can be overcome or neutralized by mechanical (large pressure drop, agitation) or electrical (opposing streaming potential) means. The model proposed here is designed to take into account the factors that work against the above repulsive forces which are responsible for the stability of the asphaltene colloidal suspension. Furthermore, with the availability of some experimental data, it may be utilized to predict the possible conditions upon which these forces are just beginning to be overcome by the van der Waals-London attractive forces between asphaltene particles, which consequently flocculate. The point at which the colloidal asphaltene particles begin to precipitate is called the *onset of asphaltene flocculation*.

The present model is an initial attempt to analytically formulate two, among many others, experimentally-verified phenomena. The first is that resin particles play a significant role in the peptization of colloidal asphaltenes, and the second is that a streaming potential is generated during oil flow containing charged colloidal asphaltene particles which, in turn, causes the particles to flocculate and precipitate out of solution.

Basically, there are three general areas of scientific endeavor upon which the model depends, and these are listed below:

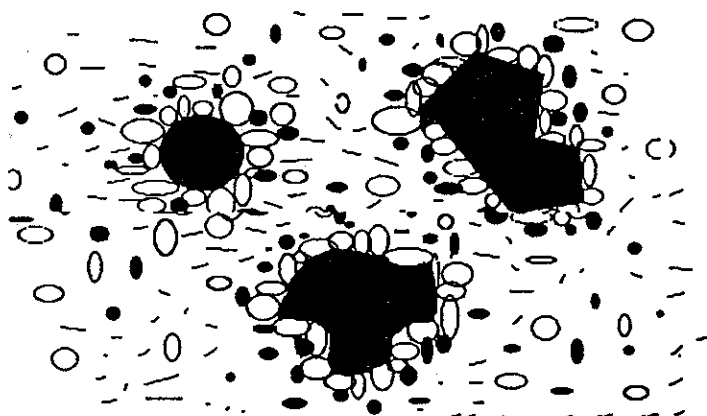
1. Resin chemical potential calculations based on the statistical mechanical theory of polymer solutions.
2. Resin adsorption on the asphaltene particle surface and Langmuir isotherm calculations and experiments, and titration experiments with different solvents to determine the onset of asphaltene flocculation.
3. Calculation of the Streaming Potential generated during the flow of charged colloidal asphaltene particles. Experimental determination of colloidal asphaltene particle charge.

At this point it is warranted to give a basic definition of what is meant by the terms resin and asphalt. Note that asphaltenes have been adequately defined previously. Resins are called a class of highly polycyclic molecules that exist in the oil in true solution, they are

easily adsorbed in common adsorbents like clay or silica gel, and their molecular weight falls within the range of 250 to 1,000 [6, 8]. Asphalt is known as the mixture that flocculates out from oil and contains asphaltene particles surrounded by resins, oil, and other liquid entities in the crude oil that are trapped in the flocculated mass.

*A. Resin chemical potential and statistical mechanical theory of polymer solutions:*

It is currently accepted by many researchers of the asphaltene deposition problem that a portion of asphaltene particles exists in the oil in a colloidal dispersed state (in suspension) and are primarily peptized or stabilized by polymeric resin molecules that are adsorbed on their surface [3, 6-10], see Fig. 1. The other portion of the asphaltenes in oil is believed to be dissolved [13, 14]. To date, there exist two theories that account for the stability of colloidal dispersions; the *DLVO theory* and the *steric stabilization theory* [16-18]. The DLVO theory is applicable to electrolytic systems, where stabilization is due to the electrical double-layer. The steric stabilization theory is applicable to systems where the dispersed phase (particulate phase) is stabilized by repulsive interactions between molecules adsorbed on the surface of the suspended particles. Based on the nature of asphaltene particles and the other contents of the petroleum fluids, it is believed that the colloidal asphaltene dispersions in oil belong to the latter (steric) category.



**NOTES**


- 1.0 ○ represents resin molecules
- 2.0 ● represents aromatic molecules
- 3.0 — represents oil molecules of different size and paraffinic nature
- 4.0  represents asphaltene particles of different sizes and shapes

Fig. 1. Asphaltene particle peptization.

The amount of resins adsorbed on the surface of colloidal asphaltenes is primarily a function of the resin concentration in the liquid phase (the oil). Therefore, for a given system (i.e., fixing the type and amount of oil and asphaltenes), changing the concentration of resins in the oil will cause the amount of resins adsorbed on the colloidal asphaltene surface to change accordingly. This means that the concentration of resins in the oil can be dropped to a point at which the amount of resins adsorbed is insufficient to cover the entire surface of colloidal asphaltenes, and this will permit the colloidal asphaltene particles to aggregate, grow in size, and eventually flocculate. Since desorption of the resins from the surface is necessary for aggregation and flocculation to occur, this may be what happens when miscible solvents are added to a crude oil and precipitation of asphaltenes takes place.

According to the principle of phase equilibria, a necessary condition for chemical equilibrium between two phases is that the chemical potential of each component in one phase is equal to its chemical potential in the other phase. Writing this condition for the resins in the asphaltene and oil phases, we will have:

$$\mu_{resin}^{asphaltene\ phase} = \mu_{resin}^{oil\ phase} \quad (1)$$

Calculation of the chemical potential of the resin in the solid phase would require utilizing small system thermodynamics techniques. However, the model requires only calculation of the chemical potential of the macroscopic asphaltene-free oil phase and, as a result, macroscopic chemical potential calculations are adequate.

The Flory-Huggins statistical mechanical theory [19, 20] permits calculation of the chemical potential of a large molecule-like resin (or any polymeric molecule or macromolecule) through the following equation:

$$\Delta\mu_R/RT = [\mu_R - (\mu_R)_{ref}]/RT = \ln(\Phi_R) + 1 - v_R/v_m + \chi_R \quad (2)$$

Where  $\Phi_R$  is volume fraction of resin in the liquid,  $v_R$  and  $v_m$  are molar volume of resin and liquid mixture, respectively,  $\chi_R = (v_R/RT)(\delta_m - \delta_R)^2$  is the Flory-Huggins interaction parameter,  $\delta_R$  is resins solubility parameter and  $\delta_m = \sum \Phi_i \delta_i$  and  $v_m = \sum x_i v_i$  are the solubility parameter and molar volume of the asphaltene-free oil mixture, respectively. There exist more elaborate statistical mechanical expressions for the chemical potential of a polymeric molecule in a solution in which more structural details of the intra- and intermolecular characteristics of the polymers are taken into account [14, 19]. However, the reason for the use here of the Flory-Huggins statistical mechanical theory to perform the chemical potential calculation of the resin in the liquid is due to its simplicity.

Let us call the point at which the concentration of resins in the liquid is just enough to keep the colloidal asphaltene particles completely covered with resin molecules as the

*critical resin point* and the concentration of the resins in the liquid phase as the *critical resin concentration*,  $(C_R)_{crit}$ . At this concentration we can calculate the critical chemical potential,  $(\Delta\mu_R)_{crit}$ , of the resins in the liquid mixture which, of course, is equal to the chemical potential of the resins in the solid phase. The significance of this is that we can change the nature of the liquid mixture (i.e., add or remove miscible solvent) as we wish and as long as the calculated chemical potential remains equal to or above the critical chemical potential, the colloidal asphaltene particles will remain completely covered. This is another way of saying that it is the chemical potential of the resins in the solid and the liquid phases that determines their split between the two phases.

The basic concept here is that, at the onset of colloidal asphaltene deposition, the solid phase arrives at the same physical state, which is colloidal asphaltene particles just covered with resins, regardless of what the composition of the liquid phase is. So, if the critical chemical potential is known at one liquid composition, then it is known (it is the same) for all other compositions, provided that the temperature remains constant and the pressure stays above the bubble point of the mixture. The effect of temperature on resin adsorption and as a result on the critical chemical potential is discussed later in this paper. Pressure does not appear directly into the resin chemical potential expression, as it can be seen from Eq. 2 above. However, it does enter into the flash calculation performed to determine the liquid phase composition of the oil mixture. It is the liquid composition that is used in determining the resin chemical potential.

It appears from the above discussion that  $(C_R)_{crit}$  is an important parameter for every crude oil mixture. Actually, what we are looking for is the liquid chemical potential of the resins that corresponds to the point at which the colloidal asphaltene particles are just completely covered with resins. The determination of  $(C_R)_{crit}$  is discussed in the next section. It is important to note here that the addition of light paraffins to an oil mixture will tend to make the chemical potential of the resins in the liquid smaller (see Eq. 2) which, of course, will result in desorption of the resins from and the subsequent aggregation and flocculation of the colloidal asphaltene particles.

Given the  $(C_R)_{crit}$  of a particular oil mixture, i.e., a reservoir fluid, we can compare it to its actual  $C_R$  and, depending on which is larger, we can deduce whether the subject reservoir fluid is prone to colloidal asphaltene deposition during its production from the ground. If  $C_R < (C_R)_{crit}$ , flocculation is possible and its extent will depend on how much smaller  $C_R$  is than  $(C_R)_{crit}$  and on the production techniques used, which will be discussed later in this report. In the case of  $C_R > (C_R)_{crit}$ , we can actually calculate the amount of solvent (i.e., heptane, pentane, propane,  $CO_2$ ) that can be added to the oil mixture without getting into the colloidal asphaltene flocculating condition. The method is summarized below:

- a. Using  $(C_R)_{crit}$  and resin and oil properties, calculate the critical chemical potential of

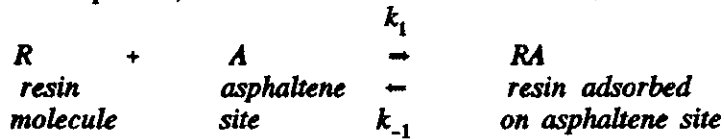
the resins,  $(\Delta\mu_R)_{crit}$ , using Eq. 2.

b. By trial and error, calculate the amount of solvent that must be added to bring the resin chemical potential in the oil mixture down, equal to  $(\Delta\mu_R)_{crit}$ .

c. The solvent added in step b. is the maximum allowed to be added to the subject reservoir fluid, without getting into the colloidal asphaltene flocculation range.

**B. Resin adsorption-Langmuir isotherm - determination of  $(C_R)_{crit}$  by adsorption experiments:**

The Langmuir isotherm equation can be derived [21, 22] by representing the adsorption process as a chemical equation, i.e.:



At equilibrium we have  $K = k_1/k_{-1} = x_{RA}/x_A C_R =$  equilibrium constant where  $C_R$  is the concentration of resins in the liquid,  $x_A$  is the fraction of vacant sites on colloidal asphaltene particles and  $x_{RA}$  is the fraction of occupied sites on colloidal asphaltene particles. Since,  $x_{RA} = 1 - x_A$ , we have  $K = x_{RA}/(1 - x_{RA})C_R$  and, finally, we have:

$$x_{RA} = KC_R / (1 + KC_R) \quad (4)$$

Let us define  $m$  as the weight of resins adsorbed per unit weight of asphaltenes by the following equation:

$$m = bx_{RA} \quad (5)$$

Where  $b = m$  at  $x_{RA} = 1$  (at complete occupancy of all asphaltene particle sites). By replacing Eq. 4 in Eq. 3, we get  $m = bKC_R/(1 + KC_R)$  which, upon rearrangement, yields:

$$1/m = 1/b + 1/bKC_R \quad (6)$$

Provided experimental data of  $m$  vs  $C_R$  are available,  $1/m$  vs  $1/C_R$  could be plotted, and by applying Eq. 5 the equilibrium constant  $K$  would be obtained. It is then possible to utilize Eq. 3 to make a plot of  $x_{RA}$  vs  $C_R$ , which would generally look like Fig. 2. From such a figure  $(C_R)_{crit}$  can be read at  $X_{RA} = 1.0$ .

**Determination of  $(C_R)_{crit}$  by titration experiments:**

Determination of the onset of asphaltene flocculation of an oil mixture by titration using a miscible solvent (i.e., pentane, heptane, decane, etc.) is performed routinely in asphaltene deposition studies [13, 15]. The method involves the addition of different amounts of a miscible solvent to a crude oil sample and the visual determination of the point of flocculation. Magnification through the use of a microscope may help in making more

accurate observations. Other indirect techniques may be utilized through which the onset of asphaltene deposition can be detected without the need of direct observation of the precipitate, which could prove quite difficult, as in the case of heavy petroleum crudes. One such method using interfacial tension measurements as a function of amount of solvent added has been studied and proposed here, at the University of Illinois [23]. The composition of the oil-solvent mixture at the onset is used to calculate the *critical chemical potential* of the oil mixture.

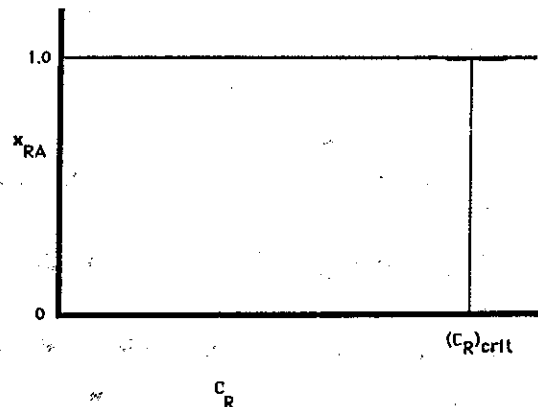


Fig. 2. Langmuir isotherm for asphaltene particles permitting determination of  $(C_R)_{crit}$ .

*Temperature effect on  $(C_R)_{crit}$  or critical chemical potential:*

In the absence of the equilibrium constant data for resin adsorption on the surface of asphaltene particles for calculating the critical chemical potential of the oil mixture, implementation of the proposed model will require some experimental data of the onset of asphaltene deposition for fitting purposes. The model can then be used to predict the onset at different liquid compositions, provided that the resin and asphaltene fractions remain as they were when the fitting point was determined. Since the temperature is a parameter in Eq. 2, it is preferable to obtain the experimental onset point at the temperature that we need to predict the onset. This is a typical case of using stock tank oil to get the experimental onset point and, based on this data point, predicting the onset of asphaltene flocculation of the original reservoir fluid.

When the temperature of the reservoir is too high to permit a practical determination of the onset of asphaltene flocculation of the stock tank oil with a given solvent, then the following expression may be used to extrapolate  $(C_R)_{crit}$  to reservoir temperature:

$$[(C_R)_{crit}]_{T_2} = [(C_R)_{crit}]_{T_1} \times (\alpha) [(T_2 - T_1)/T_2 T_1] \quad (7)$$

where:  $\alpha$  is a constant determined using two experimental onset data points at two different



temperatures. This equation is derived from Eq. 6 by assuming an Arrhenius temperature dependency [24] for the equilibrium constant,  $K$ , i.e.:

$$K = K' e^{w/kT} \quad (8)$$

Where  $w$  is the energy of adsorption,  $k$  is the Boltzman constant and  $K'$  is a constant. The  $(C_R)_{crit}$  calculated from Eq. 7 at the reservoir temperature may be used to calculate the critical chemical potential of the reservoir fluid, which in turn is used to calculate the onset of asphaltene deposition of the reservoir fluid with any given solvent. Since the determination of constant  $\alpha$  in Eq. 7 requires two different experimental onset data at different temperatures, it is preferable, where possible, to perform only one titration at the reservoir temperature, thus eliminating the need to extrapolate to a different temperature.

### C. Electrokinetic phenomena during asphaltene deposition

As discussed previously, when the concentration of resins,  $C_R$ , in an oil containing colloidal asphaltenes is smaller than the critical concentration of resins,  $(C_R)_{crit}$ , for that particular oil mixture aggregation and flocculation of colloidal asphaltene particles may occur. Flocculation would occur because the particles could approach each other at their uncovered area and coagulate. This process may be assisted by mechanical and thermal mixing effects, i.e., large pressure and/or temperature changes. The question that arises at this point is whether the similar charge on the unsaturated colloidal asphaltene particles could work to oppose their flocculation. The answer is affirmative, which may explain why colloidal asphaltenes would not flocculate out of a reservoir fluid when left in place. However, when the oil is being produced, another phenomenon may enter into the picture and that is the generation of a *streaming potential*, which is a phenomenon that is expected to occur when colloidal liquid mixtures are in transit [16-18].

It has been proven experimentally that asphaltenes will flocculate out of solution when placed under the influence of an electrical field [2, 3]. When the streaming potential generated during flow of oil through reservoir pores, well tubings and pipes is large enough, it could assist in flocculating asphaltenes through electrodeposition [11]. It is therefore necessary to establish the quantitative tools that would permit us to calculate the magnitude of the generated streaming potential during the flow of oil.

#### C.i Charge of asphaltene particles:

In this section, the basis for formulation of the electrokinetic equations of sterically stabilized colloidal suspensions is presented. It should be pointed out that, since the steric theory differs from the DLVO theory of colloidal suspensions, there is no parallel between the derivation of the present equations with those based on the DLVO theory. As mentioned previously, the DLVO model does not apply in the non-electrolytic oil-asphaltene system. The expression for the streaming potential equation will be developed by considering the

transport of asphaltenes during the flow of asphaltenes containing oil as electrical charges in transit. This is really a simplified view, but one that clearly agrees with the conventional definition of electrical current as *electrical charges in transit*. Let us consider Fig. 3, in which the flow of oil containing charged asphaltene particles in a conduit is depicted. The following points may be made regarding this flow system:

- a. Transfer of charged asphaltene particles with the flow of oil is equivalent to a net current or a *streaming current* and therefore to a potential difference. This potential difference opposes the mechanical transfer of charge.
- b. For the system shown in Fig. 3, where the particles are positively charged, the potential is set up as a negative upstream and positive downstream, if it is to oppose the flow of the charged asphaltene particles.
- c. This potential difference causes the particles to tend to flow backwards or it may be said that it causes back conduction by ion diffusion (asphaltene particle upflow diffusion) and/or, to a much lesser extent, by electro-osmosis. The charge transfer due to back-conduction and electro-osmosis is called *leak current*.
- d. At the condition when the asphaltene particles tend to remain stationary because of the balance between the two opposing forces, the potential difference is called *streaming potential*.
- e. Using an electrophoretic cell, the *charge* of the asphaltene particles may be determined experimentally. The expression which may be utilized for this purpose is the following [16]:

$$Q_{part.} = \text{charge of particle} = 6\pi\mu au/E \quad (9)$$

where  $Q$  is the net charge on colloidal asphaltene particle,  $E$  is the electric field strength,  $\mu$  is viscosity of the medium,  $a$  is the radius of the particle and  $u$  is the electrophoretic velocity of the particle.

For electrolytic systems the charge of the particle is related to its zeta-potential by the following equation:

$$Z = Q/(4\pi Da) \quad (10)$$

where  $Z$  is the zeta potential and  $D$  is permittivity (or dielectric constant) of oil. From Eqs. 9 and 10 we get [16]:

$$Z = 1.5\mu u/DE \quad (11)$$

Charge is an important property of colloidal asphaltene particles in transit and is utilized in the next section to calculate their streaming potential.

#### C.ii Streaming potential equation:

As mentioned before, the *streaming potential* is that potential difference developed along

the flow path at which the *streaming current* and the opposing *leak current* are equal. The governing equations for each current can be developed as follows:

a. **Streaming current:** Figure 4 illustrates the physical model that is visualized for the development of the equations associated with the streaming current. By designating the charge density per unit volume in the oil due to the charged asphaltene particles as  $\rho_c$  and the rate of flow of oil as  $Q$ , then the streaming current,  $I_s$ , due to the flow of the asphaltene particles, will be given by:

$$I_s = \int_0^R \rho_c dQ \tag{12}$$

By referring to Fig. 4, we can see that:

$$dQ = 2\pi r u_r dr \tag{13}$$

is the flow rate through the cylindrical layer of thickness  $dr$ .

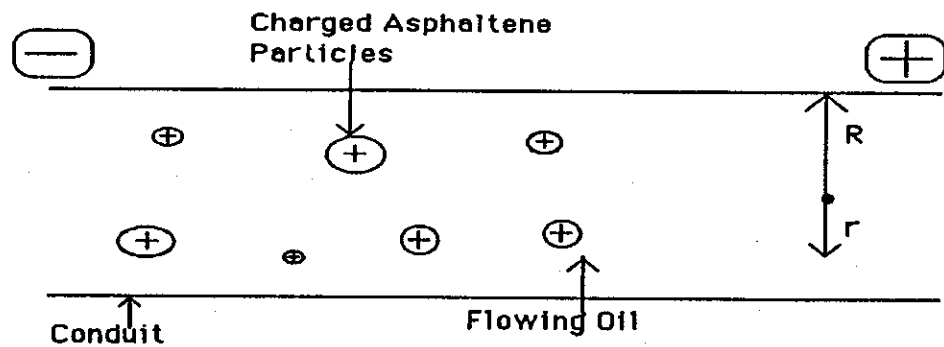


Fig. 3. Streaming potential generated by the flow of oil containing charged asphaltene particles.

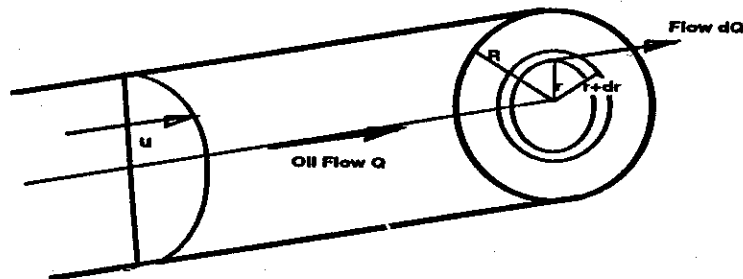


Fig. 4. Development of streaming current equation.

Since the Poiseuille equation for laminar flow is:

$$u_r = \Delta P (R^2 - r^2) / 4\mu L \quad (14)$$

By substituting Eq. 14 in Eq. 13, one obtains:

$$dQ = 2\pi r [\Delta P (R^2 - r^2) / 4\mu L] dr \quad (15)$$

Now, by substituting Eq. 15 into Eq. 12 and assuming that  $\rho_c$  is a constant, the following is obtained:

$$I_s = [\Delta P \pi \rho_c / 2\mu L] \int_0^R (R^2 r - r^3) dr$$

which, upon integration, gives the equation for the streaming current:

$$I_s = \Delta P \pi \rho_c R^4 / 8\mu L \quad (16)$$

b. Leaking current: The leaking current due to a streaming potential E is given by [16-18]:

$$I_L = E/R = E(A/\rho_r L) = Ek(A/L) = Ek(\pi R^2/L) \quad (17)$$

where R is the resistance of oil and pipe wall,  $\rho_r$  is the resistivity of the oil and pipe wall, A is the area of the flow channel, L is the length of the flow channel and k is the conductivity of the oil and pipe wall.

Since at steady state the streaming and leaking currents are equal from equating Eqs. 16 and 17, the following is obtained:

$$E/\Delta P = \rho_c R^2 / 8\mu k \quad (18)$$

This expression holds for laminar flow. In terms of the average velocity in the conduit, this equation can be modified by using the classical pressure drop equation for laminar flow:

$$\Delta P/L = 32\mu u_{avg} / d^2 = 8\mu u_{avg} / R^2$$

Substitute Eq. 19 into Eq. 18 to get:

$$E = \rho_c u_{avg} L / K \quad (20)$$

This is the final equation for calculating the streaming potential in a laminar flow regime.

For a turbulent flow regime, the following equation is suggested [25]:

$$\Delta P/L = 0.1584\rho^{0.75}\mu^{0.25}u_{avg}^{1.75}/d^{-1.25} \quad (21)$$

By substituting Eq. 21 into Eq. 18, and after some algebraic manipulations, one obtains:

$$E = 4.95 \times 10^{-3} (\rho_c d^{0.75} L \rho^{0.75} / \mu^{0.75} k) u_{avg} \quad (22)$$

This is the final equation for calculating the streaming potential in the turbulent flow regime. In order to check whether a flow is laminar or turbulent, the Reynold's number

$$Re = du_{avg} \rho / \mu \quad (23)$$

will be used. For laminar flow  $Re = (1 \text{ to } 2100)$  while, for turbulent flow,  $Re > 2100$ .

*Expression for  $\rho_c$ :*

The term  $\rho_c$ , appearing in Eq. 22, must be expressed in terms of some measurable quantities. Knowing that

$$\begin{aligned} \rho_c &= (\text{total charge})/\text{unit volume of oil} \\ &= [(\text{charge per particle})(\# \text{ of particles})]/(\text{unit volume oil}) \end{aligned}$$

Let us make the following designations:

$$\begin{aligned} W_p &= \text{mean weight of colloidal asphaltene particles} \\ q_p &= \text{mean charge on colloidal asphaltene particles} \\ V_p &= \text{mean volume of colloidal asphaltene particles} \\ d_p &= \text{mean diameter of colloidal asphaltene particles} \\ W_T &= \text{total weight of asphaltenes in unit volume of oil} \\ W_A &= \text{weight \% of colloidal asphaltenes in oil} \\ \rho_A &= \text{mean density of colloidal asphaltenes} \end{aligned}$$

then we have:

$$W_T = W_A \rho_{oil} \quad (24)$$

$$\rho_c = q_p (W_T / W_p) \quad (25)$$

By substituting Eq. 24 into Eq. 25, one gets:

$$\rho_c = q_p \rho_{oil} (W_A / W_p) \quad (26)$$

also knowing that

$$W_p = \rho_A (\pi d_p^3 / 6) = \rho_A V_p \quad (27)$$

Eq. 27, when replaced into Eq. 26, will produce:

$$\rho_c = q_p \rho_{oil} (6 W_A / \rho_A \pi d_p^3) \quad (28)$$

This is the final equation that expresses  $\rho_c$  in terms of the measurable quantities appearing

in the right-hand side of the equation. This equation may be used in conjunction with Eqs. 20 and 22. For instance, combining Eq. 28 with Eq. 22, the expression for the streaming potential in a turbulent flow regime will be produced as the following:

$$E = (0.0297 / \pi) [(q_p W_A / d_p^3 \rho_A) (d^{0.75} L \rho_{oil}^{1.75} / \mu^{0.75} k)] u_{avg}^{1.75} \quad (29)$$

Overall electrical conductivity,  $k_{tot}$  :

In Eq. 29,  $k$  is the overall electrical conductivity of the oil and the wall of the conduit. With respect to the electric current, the following can be written:

$$I = E k_{tot} (A / L) \quad (30)$$

In the present situation, we have:

$$I = E [k_{oil} (A_i / L) + k_{wall} ((A_e - A_i) / L)] = (EA_i / L) [k_{oil} + k_{wall} (d_e / d_i - 1)] = (EA_i / L) k_{tot} \quad (31)$$

Comparing Eq. 31 with Eq. 17, we see by analogy that  $k$  in Eq. 29 is given by:

$$k_{tot} = k_{oil} + k_{wall} (d_e / d_i - 1) \quad (32)$$

The pipe wall, in this case, acts like a *short circuit* since it conducts current back to the pipe entry point and lowers the value of  $E$ .

### 3. COMPARISON OF EXPERIMENTAL DATA WITH MODEL PREDICTIONS

It was said earlier that oil mixtures can exist either above or below their  $(C_R)_{crit}$  without flocculation of colloidal asphaltenes. The stabilizing forces in each case are assumed to be the repulsive forces between resins adsorbed on different colloidal asphaltene particles and repulsive electrical forces due to the similar electric charge on the colloidal asphaltene particles. In the first case, when  $(C_R) > (C_R)_{crit}$ , addition of a solvent may bring the resin concentration below  $(C_R)_{crit}$ , which will be identical to the second case. In the second case, when  $(C_R) < (C_R)_{crit}$ , adequate agitation or streaming potential generated during flow of oil in porous media or conduits may cause colloidal asphaltene flocculation. In this section, a comparison of the available experimental data with predictions by the proposed model is reported.

Table 1 contains the experimental and predicted onset data of asphaltene flocculation using different miscible solvents. The experimental onset data are for tank oil no. 1 reported in Ref. [13]. Also reported in Table 1 are the results of three computer runs based on the present model, assuming that the entire asphaltene content of tank oil no. 1 is colloidal asphaltenes only. In each computer run one set of experimental onset data is used for fitting

to the model and the rest are predicted. It should be pointed out that the heptane fitted run makes the worst predictions while the hexadecane and dodecane fitted runs make rather good predictions.

Table 1. Experimental [13] and predicted onset data.

1. Hexadecane experimental onset used for fitting the model. Amount of hexadecane added at the onset is 75.3 moles.				
Solvent	Predicted onsets		Experimental onsets	
	moles	cc/gm oil	moles	cc/gm oil
pentane	309	1.6	---	>1.3
heptane	169	1.1	210	1.4
decane	158	1.4	158	1.4
dodecane	124	1.3	125.8	1.3
2. Dodecane experimental onset used for fitting the model. Amount of dodecane added at the onset is 125.8 moles.				
Solvent	Predicted onsets		Experimental onsets	
	moles	cc/gm oil	moles	cc/gm oil
hexadecane	76.3	1.0	75.3	1.0
pentane	316	1.7	---	>1.3
heptane	172	1.2	210	1.4
decane	160	1.4	158	1.4
3. Heptane experimental onset used for fitting the model. Amount of heptane added at the onset is 210 moles.				
Solvent	Predicted onsets		Experimental onsets	
	moles	cc/gm oil	moles	cc/gm oil
decane	194	1.72	158	1.4
dodecane	150	1.55	125.8	1.3
hexadecane	92.3	1.23	75.3	1.0
pentane	349	1.83	---	>1.3

#### Experimental and predicted streaming potentials:

The published experimental data on generated streaming potentials during flow of asphaltene containing oil are rather meager. The sample calculations presented here are performed for a typical Prinos well [2]. A Prinos well was chosen because well design and flow data were available to the authors. The Prinos oil suffered a great deal of asphaltene flocculation during primary production, which is an indication that its  $(C_R)_{\text{actual}}$  was less than its  $(C_R)_{\text{crit}}$  and, as a result, electrokinetic effects must have played the major role in the colloidal asphaltene deposition process.

*Sample calculation of streaming potential for a Prinos well:*

Let us make a streaming potential calculation for a typical Prinos well using Eq. 29. The well data are taken from reference [2] which are as the following:

$\rho_A = 1.22\text{g/cm}^3$ ,  $W_A = 4.5\text{ wt\%}$ ,  $L_{\text{tubing}} = 3000\text{m}$ ,  $(d_{\text{tubing}})_{\text{int}} = 0.07594\text{m}$ ,  $(d_{\text{tubing}})_{\text{ext}} = 3.5\text{in}$ ,  $T_{\text{avg}} = 200^\circ\text{F}$ ,  $\text{Sp.Gr.} = 0.88$  (at  $T_{\text{avg}}$ ),  $\mu = 0.58\text{cp}$ ,  $k_{\text{oil}} = 3 \times 10^{-13}(\text{ohm})^{-1} \text{cm}^{-1}$ ,  $k_{\text{wall}} = 5.0 \times 10^6(\text{ohm})^{-1} \text{m}^{-1}$ ,  $\epsilon = 2.13 \times 8.854 \times 10^{-12} \text{kg}^{-1} \text{m}^{-3} \text{s}^4 \text{A}^2 = \text{permittivity of oil}$ .

It is also assumed that  $u_{\text{avg}} = 1.840\text{m/sec}$ , which corresponds to a well production rate of  $30\text{m}^3/\text{hr}$ , and is typical for a Prinos well during asphalt deposition [2].

Parameters  $q_p$ ,  $d_p$  and  $Z$  are taken from reference [3] and are as follows:  $q_p = 15 \times 10^{-19}$  Coulombs,  $d_p = 2700 \text{ \AA} = 2.7 \times 10^{-7} \text{ m}$  and  $Z = 420\text{mV}$ .

Also, let us perform a calculation for two ideal situations: (a) Assuming no wall conductance (when tubing has insulated joints). (b) Assuming wall conductance and taking the wall thickness as uniform. In reality the wall thickness will vary because of pipe threading, rust, etc. This calculation will give a range of streaming potential. The actual streaming potential is expected to lie somewhere between the two calculated values.

*(i). Without wall conductance:*

In this case,  $k_{\text{total}} = k_{\text{oil}} = 3 \times 10^{-11}(\text{ohm})^{-1} \text{m}^{-1}$ .

Substituting  $k_{\text{total}}$  into eq. 29 one gets:

$$E = 4.32 \times 10^{16} \text{ Volts !!!!!}$$

So, it is assumed that no wall conductance gives a very high value of generated streaming potential.

*(ii). With wall conductance:*

In this case knowing  $k_{\text{total}}$  and  $k_{\text{oil}}$  and using Eq. 32, one can calculate

$$k_{\text{total}} = 3 \times 10^{-11} + 5.0 \times 10^6 [(3.5/2.992)^2 - 1] = 1.842 \times 10^6(\text{ohm})^{-1} \text{m}^{-1}$$

Then, by substituting  $k_{\text{total}}$  into Eq. 29, the following is obtained:

$$E = [(4.4617 \times 10^5)(1.840)^{1.75}] / (1.842 \times 10^6) = 1.30 \text{ Volts}$$

As can be seen, the pipe wall conductance can make a dramatic difference in the calculated streaming potential  $E$ . The actual value of  $E$  for this well is expected to be larger than 1.3 Volts for the reasons mentioned in the text, i.e., grease in the pipe joints, rust, wall thickness reductions, etc. Depending on such factors, the streaming potential can vary between the two limits reported here.

Electrodeposition experiments [3] have shown that 120 Volts of applied voltage were



enough to generate movement of asphaltene particles. The above calculation shows clearly that with 120 Volts, or even higher, generated streaming potential was a very distinct possibility for a Prinos well, especially when the tubing was corroded. Considering that rust and tubing deterioration was a major problem in Prinos because of the  $H_2S$  present in the oil, and also the fact that asphaltene deposition occurred below the bubble point in the tubing (i.e., no composition change in the oil), the calculated high generated streaming potentials seem to be a plausible explanation.

Another point of interest is that the asphaltene particle average diameter used in this calculation is 2700 Å as reported in reference [3]. Considering that asphaltenes in the original Prinos oil (not precipitated and redissolved in solvent) may have a diameter as small as 40 Å [7], it is apparent from Eq. 29 that the actual generated streaming potential may be even higher.

#### 4. CONCLUSIONS

The present model is only one aspect of our efforts to try to develop analytical predictive techniques for the phase behavior of asphaltenes by recognizing their colloidal nature. It is well-recognized that asphaltene in crude oil exists not only in the form of colloids, but also as a mixture of colloidal and dissolved particles with large molecular weight (or size) distribution. This complex nature of asphaltene may result in its deposition inside the reservoir, in the oil well, or inside pipelines or oil processing equipment. To prevent deposition it is necessary to be able to predict the onset and amount of deposition due to various factors. In order to develop a comprehensive model for asphaltene deposition we have also to consider a number of other predictive techniques, which include the statistical mechanical theory of heterogeneous polymers, kinetic theory of FRACTAL aggregation for mixtures of miscible solvent and polydisperse asphaltene, and the principles of thermodynamics of multicomponent mixture and phase equilibria [26].

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#### NOMENCLATURE

$\mu_R$	Chemical potential of resins
$\Phi_R$	Volume fraction of resins
$v_R$	Molar volume of resins
$v_m$	Molar volume of the asphaltene-free oil mixture
$x_R$	Florry-Huggins interaction parameter of resins
$\delta_R$	Solubility parameter of resins
$\delta_m$	Solubility parameter of asphaltene-free oil mixture

$x_i$	Mole fraction of component $i$
$(C_R)_{crit}$	Volume fraction of resins in the liquid at the onset of asphaltene flocculation
$(C_R)_{actual}$	Volume fraction of resin in the liquid
$(\Delta\mu_R)_{crit}$	Chemical potential of resins at the onset
$k_1$	Adsorption rate constant
$k_{-1}$	Desorption rate constant
$K$	Equilibrium constant
$w$	Weight of resins adsorbed/weight of asphaltenes
$b$	Weight of resins adsorbed/weight of asphaltenes at complete monolayer adsorption
$\zeta$	Zeta potential, mVolts
$\rho_c$	Charge density per unit volume
$u_r$	Velocity at radius $r$
$I_s$	Streaming current, amps
$I_L$	Leaking current, amps
$\rho_r$	Electrical resistivity
$k$	Electrical conductivity
$\Delta P$	Pressure drop
$u_{avg}$	average velocity
$\rho$	Density
$d$	Diameter of conduit
$L$	Length of conduit
$w_p$	Mean weight of asphaltene particle
$q_p$	Mean charge of asphaltene particle
$V_p$	Mean volume of asphaltene particle
$d_p$	Mean diameter of asphaltene particle
$W_T$	Total weight of asphaltenes
$\rho_A$	Density of asphaltenes
$E$	Streaming potential
$D$	Permittivity of oil

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