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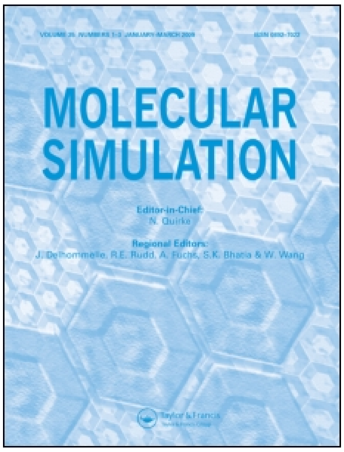

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A Simple Computational Technique for the Systematic Study of Adsorption Effects in Emulsified Systems. Influence of Inhomogeneous Surfactant Distributions on the Coalescence Rate of a Bitumen-in-water Emulsion

German Urbina-villalba[a]; Máximo García-Sucre[a]
[a] Centro de Física, Laboratorio de Átomos, Moléculas y Campos, Instituto Venezolano de Investigaciones Científicas (IVIC), Caracas, Venezuela

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A SIMPLE COMPUTATIONAL TECHNIQUE FOR THE SYSTEMATIC STUDY OF ADSORPTION EFFECTS IN EMULSIFIED SYSTEMS. INFLUENCE OF INHOMOGENEOUS SURFACTANT DISTRIBUTIONS ON THE COALESCENCE RATE OF A BITUMEN-IN-WATER EMULSION

GERMAN URBINA-VILLALBA* and MÁXIMO GARCÍA-SUCRE

Centro de Física, Laboratorio de Átomos, Moléculas y Campos,
Instituto Venezolano de Investigaciones Científicas (IVIC), Aptdo. 21827,
Caracas, Venezuela

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In order to study the evolution of a bitumen-in-water (B/W) emulsion with time, a modification of a standard Brownian Dynamics (BD) algorithm was made. In these calculations, the 3-D movement of emulsion drops is mimicked by a combination of a steady DLVO (Derjaguin-Landau-Verwey-Oberbeek) inter-drop force and a random kick. The electrostatic component of the DLVO potential is allowed to depend on the surfactant population at the interface of each drop. Surfactant adsorption changes with the total surfactant concentration of the system, the available interfacial area, and the initial spatial distribution of amphiphilic molecules. Depending on these variables, the drops can flocculate and coalesce with either real drops or periodic-boundary images. As a consequence of coalescence, the interfacial area diminishes and surfactant is re-distributed among the surviving drops. The results are compared with well-known analytical equations developed for much simpler cases. With the present simulation technique, the exponential decrease of the number of drops with time reported for B/W systems can be reproduced. Evidence of a monotonic relationship between the total interfacial area of the surviving drops and the total surfactant concentration is also presented.

Keywords: Emulsions; Bitumen; Stability; Simulations; Brownian Dynamics; Coalescence; Flocculation

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*Corresponding author. e-mail: guv@pion.ivic.ve

1. INTRODUCTION

Bitumen emulsions can be purposely produced as an alternative source of energy [1] or spontaneously generated during bitumen extraction with hot water [2]. These emulsions can be stabilized by either natural or synthetic surfactants. Surfactants adsorb to the oil/water interface, generating a strong repulsion between droplets, which in the case of ionic surfactants is essentially electrostatic in nature. At small inter-drop distances, surfactants delay the drainage of the thin liquid film that forms between drops. These effects produce a kinetic stabilization of the emulsion that allows it to withstand long periods of transportation, until it is burned or can be further treated for other commercial purposes. Since bitumen usually has a very high viscosity and a relatively high density, the prediction of de-stabilization times is crucial for the estimation of storage and transportation times.

Experimental estimations of coalescence rates are usually expensive, time-consuming, and severely restricted to a selected range of physicochemical conditions. On the other hand, the available analytical treatments are generally restricted to mono-disperse distributions of drops in relatively dilute emulsions [3–5]. Thus, formalisms significantly deviate from the experimental data of high-content bitumen/water emulsions under static conditions or subject to action of a shear stress [6]. Furthermore, most theories that address the time evolution of an emulsified system, usually start from the estimation of a collision probability of a drop submerged in a homogeneous dispersion, avoiding the prediction of the initial Drop Size Distribution (DSD) resulting from emulsification. The importance of the initial DSD is well illustrated in a recent work of Sánchez *et al.* [7] on sunflower oil emulsions. They had reported de-stabilization times between 4–10 days for 75% wt sunflower-oil/water emulsions prepared at agitation speeds between $1.7-2.5\,\mathrm{s}^{-1}$, while similar emulsions prepared at slightly higher propeller speeds ($3.3-5.0\,\mathrm{s}^{-1}$), did not show any phase separation after one-month aging.

When oil and water are stirred together in a blender, the breakage of drops is favored by the action of the impeller, while their coalescence is enhanced by convection. The resulting DSD depends on the density of the phases, the volume fraction of the disperse phase, the o/w interfacial tension, and the impeller diameter and speed [7–11]. This complexity prevents the complete theoretical prediction of the initial DSD. The final distribution of components after mixing will determine the emulsion dynamics that follows. Since the initial DSD is produced under severely inhomogeneous conditions, gradients of surfactant concentrations are very likely to exist for a few minutes after emulsification, specially in industrial mixers, where stirring times cannot be too long due to energetic costs. This time scale is of the same order of magnitude than surfactant adsorption times [12–15]. Therefore, a substantial number of drops may collide in the first few minutes before they achieve complete surfactant coverage at the interface. As a consequence, coalescence may happen shortly after emulsification even in the presence of a total surfactant concentration higher than that required for complete stabilization of the initial DSD. As will be shown in this study, computer simulations can address these complex cases, being a good alternative to expensive experimental studies, as well as analytical evaluations, which are severely restricted to a limited range of working conditions. This report presents a novel computational technique suitable for the estimation of flocculation and coalescence rates in emulsified systems. This technique is based on a slight modification of the standard Brownian Dynamics simulation algorithm.

2. EMULSION STABILITY SIMULATIONS

Computer simulations on floc formation were used as early as 1963 [16], in order to explain the large sediment volume of silica sols in organic media. Those calculations employed a simple model of successive random addition of individual spherical particles around a fix position. More sophisticated two-dimensional simulations in which randomly selected particles were aggregated and their aggregates "compacted" through subsequent rotations, had proved successful in reproducing Smoluchowski's variation of the number of N-particle aggregates with time [17]. Models as simple as hard-spheres and pearl-necklace polymers with a sticking probability, had proved useful for the calculation of the fractal properties of aggregates formed by the complex phenomena of bridging flocculation [18, 19].

More elaborate techniques for colloidal simulation including the explicit movement of particles as a function of time, are also published. Computer simulations of impact flocculation between wet rotating particles interacting through capillary forces under the action of gravity are available [20]. Mitchell *et al.*, reported Brownian Dynamics simulations of near-hard spheres under shear ($V \propto (\sigma'/r)^n$; $n = 36$) [21]. Their calculations used 108, 122, 256, 500, 1372 and even 4000 particles, to evaluate the theoretical structure factor of sheared systems, and even the intensity spectra of the resulting particle distribution.

Brownian dynamics simulations of mono-dispersed distributions of 864 Lennard-Jones particles had been successfully used for studying the gas/liquid phase separation and its similarities with the process of gel formation [22]. Segre *et al.* [23], had included hydrodynamic interactions in the movement of hard sphere particles, by coupling Brownian dynamics with Lattice Boltzmann techniques. Those calculations are probably the state of the art in the detailed mesoscopic description of the solvent influence upon Brownian movement.

In the present calculations have used a modification of a standard BD algorithm [24]. As usual, the position of each particle in one-dimension is given by:

$$X_{i+1} = X_i + \left(\frac{DF}{kT}\right)\Delta t + \mathrm{Ran}^{*}\sqrt{2D\Delta t} \tag{1}$$

where: X_i is the position of a particle at time "i", D is the diffusion constant, F the driving force, k is the Boltzmann constant, T the temperature, Δt, the time step and "Ran" is a Gaussian random function with zero mean and unit variance. This random variable summarizes the effect of millions of collisions of the solvent molecules with the particle surface. The result is a thermal "kick" in a random direction, lower or equal to $\sqrt{2D\Delta t}$.

A complete simulation of emulsion stability requires the inclusion of DLVO (Derjaguin-Landau-Verwey-Oberbeek) [25, 26–29], steric, gravitational and hydrodynamic contributions, in the driving force "F" (Eq. (1)). Hydrodynamic interactions include the effects of particle movement upon the diffusion tensor (type-I interactions) [24, 30–32], as well as the effects of film drainage upon coalescence (type-II interactions) [33–35]. All the referred forces occur in the same time scale, and it is extremely difficult to decipher the DSD as a consequence of their separate influences. It is known for instance, that both types of hydrodynamic interactions slow down the coalescence rate. However, both coalescence and the hydrodynamic interactions themselves depend on surfactant adsorption. If adsorption is fast compared to the collision frequency between drops, the coalescence rate will sensibly decrease. If, on the other hand, adsorption is extremely slow, surfactant adsorption will play a minor role on the coalescence rate. Unfortunately, the vast majority of the cases fall in between these two extremes. It is for this reason that we have decided to address the most simple situation first, and add additional contributions consecutively. The present calculations only include DLVO contributions in the driving force. We concentrate on the influence that inhomogeneous surfactant distributions may have on the DSD. These calculations will serve as our standards for more involved simulations, in which a quantitative coalescence rate could be evaluated. Despite this limitation, and up to our knowledge, these are the first simulations that consider time-dependent inhomogeneous surfactant distributions among drops, with a complete DLVO potential dependent on surfactant adsorption. Furthermore, we are not aware of any other dynamic simulation in which the number of drops is allowed to decrease by coalescence with complete account of the DLVO forces involved.

Analysis of experimental data on DLVO basis is common [36, 37] but is almost invariably restricted to a comparison of the time-independent potential barriers between equal-sized drops at a given salt concentration. According to DLVO theory, the interaction between two colloidal particles is basically the result of dispersion forces between the molecules of each particle and electrostatic forces generated by surfactant adsorption. The dispersion forces are assumed to be always attractive whenever retardation effects are small, as in the case of bitumen in water emulsions. At small distances, the dispersion interaction between two spherical drops can be expressed as [38]:

$$U_{\text{dispersion}} = -\frac{A_{ij}}{6d}\frac{R_iR_j}{(R_i+R_j)} \tag{2}$$

where R_k is the radius of particle "k", A_{ij} is the Hammaker's constant, "d" is the distance between the particles' surfaces ($d = r_{ij} - R_i - R_j$), and r_{ij} the distance between the center of masses of particles i and j. As shown by Lu *et al.* [39], the singular behavior of Eq. (2) at very short distances can be avoided considering finite molecular sizes in the computation of the pair-wise additive dispersion interaction. For simplicity we have employed the usual analytical expression (Eq. (2)). This assumption is justified whenever the Hammaker constant (A_{ij}) has been deduced from critical coagulation concentration data employing Eq. (2). In these initial calculations we have not included geometric corrections for drop deformations which are unlikely to happen for small size drops of high electrostatic potentials, as considered in the present work.

Recently, Sader [40] proposed analytical formulae for the surface charge density and electrostatic potential of a particle immerse in a 1 : 1 electrolyte. That formalism is valid for wide range of Debye lengths ($1/\kappa$), keeping a good degree of accuracy for all surface potentials of practical interest (< 200 mV). The electrostatic potential of interaction between two drops (in kT units) is equal to:

$$U(r_{ij}) = \left(\frac{AB(i)B(j)}{r_{ij}}\right)[r_i\, r_j]\exp(\kappa a[r_{ij} - r_i - r_j]) \tag{3}$$

$$A = \left(\frac{4\pi kT\varepsilon\varepsilon_0 a}{e^2}\right) \tag{4}$$

$$B(i) = \left(\frac{\phi_p + 4\gamma\Omega\kappa r_i a}{1 + \Omega\kappa r_i a}\right) \tag{5}$$

$$\gamma = \tanh(\phi_p/4) \quad \Omega = \frac{(\phi_p - 4\gamma)}{2\gamma^3} \tag{6}$$

where: k is the Boltzmann constant, T the temperature, ε the dielectric constant of the medium, ε_0 the permitivity of vacuum, "a" a particle radius of reference, r_k is the radius of particle "k" in units of "a" (R_k/a), and "e" the electronic charge. The electrostatic potential at the particle's surface, ϕ_p (in units of kT/e), can be computed from its surface charge density σ employing Eq. (7):

$$\frac{\sigma e}{\kappa\varepsilon kT} = \phi_p + \frac{\phi_p}{\kappa a r_i} - \frac{\kappa a r_i[2\sinh(\phi_{p/2}) - \phi_p]^2}{[4\tanh(\phi_p/4) - \phi_p] - \kappa a r_i[2\sinh(\phi_p/2) - \phi_p]} \tag{7}$$

As shown by Eqs. (3)–(7), the electrostatic component of the inter-drop potential increases with the surface charges. For ionic surfactants and non-polar oils, the surface charge density (σ) is basically the result of surfactant adsorption, which depends on surfactant distribution and diffusion constant. As the surfactant concentration lowers, the surface charge diminishes, and the attractive part of the DLVO potential predominates. When the drops partially covered by surfactant coalesce, the available interfacial area of the emulsion diminishes, and less surfactant is required to cover the remaining drops. At a certain time, the amount of surfactant adsorbed in all drops might be enough to generate a considerable repulsive barrier toward coalescence (Fig. 1). From that point on, an abrupt decrease in the coalescence rate should be observed, and the interfacial area will remain constant as a function of time.

Equations (3)–(7) require as input the radii and diffusion constant of the drops, as well as their surface charge. The radii is usually known from laser diffraction experiments, while the diffusion constant can be either measured

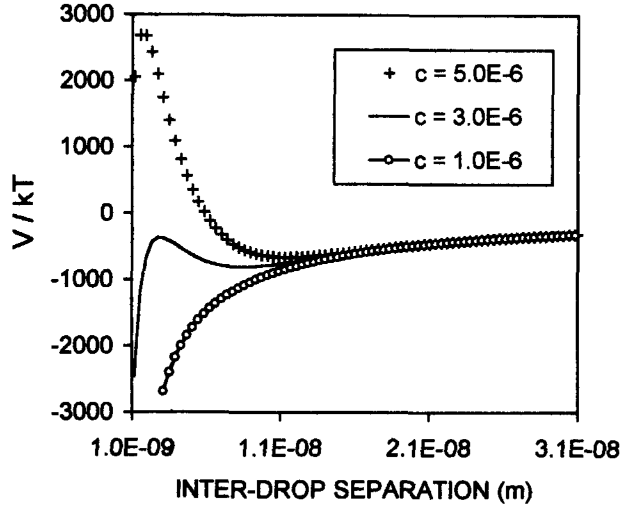

FIGURE 1 Inter-drop potential as a function of surfactant concentration. The repulsive electrostatic barrier decreases as the number of surfactants adsorbed to the surface diminishes.

or estimated from Stokes law. For emulsion stability simulations, the surface charge represents a problem because it depends on surfactant adsorption, which in turn depends on the total surfactant concentration and diffusion constant. Fortunately, ζ-potential measurements at maximum surfactant adsorption can be used in order to find out the total surface charge of a drop for a given surfactant concentration of the emulsion. Gibbs adsorption isotherm can then be used to determine the interfacial area of the surfactant at a similar concentration, if the drop curvature does not influence greatly the amount of surfactant adsorbed [41]. The ratio between the total surface area of an emulsion drop and the surfactant area at the interface, gives the number of surfactants per drop. The ratio between the total charge of the drop and the number of surfactant molecules adsorbed, gives the effective surface charge of the surfactant for a given surfactant concentration. Once the effective surfactant charge has been calculated, subsequent drop charges at different degrees of surfactant adsorption can then be estimated as the product of the number of adsorbed surfactant molecules times the effective surfactant charge. Thus, the surface charge density of a drop is:

$$\sigma = \frac{1}{A_{\text{drop}}}\left[\left(\frac{A_{\text{drop}}}{A_{\text{surf}}}\right) z_{\text{surf}}\right] \tag{8}$$

where: A_{drop} is the area of an emulsion drop, A_{surf} ($=\Gamma^{-1}$) is the interfacial surfactant area, and z_{surf} the charge of a surfactant molecule.

As soon as a new interface is formed, surfactant adsorption starts to increase due to surfactant diffusion to the interface. As it is clear from simple calculations, even at low surfactant concentration and small simulation boxes, the number of surfactant molecules required for a complete dynamic simulation of an emulsion, is huge. However, it is possible to simulate the time-dependent consequences of surfactant diffusion rather than the details of the diffusion process itself. When adsorption happens, the available interfacial area per molecule decreases causing a growth in the surface charge density of the drop. This complex process can be simulated allowing the interfacial area of the surfactant to depend on time ($A_{surf} = A_{surf}(t)$) in a way consistent with the diffusion-controlled mechanism. Since the effective surfactant area is time-dependent, the use of Eq. (8) will vary the surface charge density, and the electrostatic potential of each drop. If the usual adsorption isotherms hold out of equilibrium as claimed by Diamant and Andelman [42] for the case of diffusion-controlled adsorption, the available area per surfactant at the surface (A_{surf}) should decrease exponentially with time:

$$A_{surf} = C\Gamma_{sat}^{-1} \exp\left(\frac{(\ln(C^{-1}))(t-t_0)}{t_f - t_0}\right) \tag{9}$$

where: C is a positive number (~ 1000), t_0 the time at which surfactant diffusion starts, t_f the time needed for a surfactant to achieve surface saturation, and Γ_{sat}^{-1} is the surface excess at infinite adsorption time. The exact form of $A_{surf}(t)$ can be taken from dynamic tension measurements whenever available. Similar corrections can be introduced for kinetically-controlled adsorption:

$$\begin{aligned} A_{surf} = {} & C\Gamma_{sat}^{-1} \exp\left(\frac{(\ln(C^{-1}))(t-t_0)}{t_f - t_0}\right) S(t_f \geq t) \\ & + S(t > t_f)\Gamma_{sat}^{-1} \exp\left(\frac{(\ln(C_2^{-1}))(t-t_f)}{t_{f2} - t_f}\right) \end{aligned} \tag{10}$$

where: $S(t_1 > t_2)$ is a Heaviside-type function ($S(t_1 > t_2) = 0$ for $t_1 < t_2$; $S(t_1 > t_2) = 1$ for $t_1 > t_2$). In Eq. (10), t_f is the time required for the attainment of a steady state, Γ_{sat}^{-1} the interfacial area of the surfactant in the steady state condition, t_{f2} the time required for the final saturation of the interface, and C_2 is a positive constant chosen according to Eq. (11):

$$\Gamma_{\mathrm{sat}\,2}^{-1} = \lim_{t \to t_{f2}} \Gamma_{\mathrm{sat}}^{-1} \exp\left(\frac{(\ln(C_2^{-1}))(t - t_f)}{t_{f2} - t_f}\right) \tag{11}$$

where: $\Gamma_{\mathrm{sat}\,2}^{-1}$ is the surface area of the surfactant at saturation adsorption. Therefore:

$$C_2 = \left(\frac{\Gamma_{\mathrm{sat}}^{-1}}{\Gamma_{\mathrm{sat}\,2}^{-1}}\right) \tag{12}$$

In this way, a detailed description of the diffusion process is avoided, but its consequences on the effective potential between drops, are still taken care of. It is clear that similar procedures can be employed for processes as complex as Ostwald ripening [29]. In that case, the transfer of matter from small to large drops can be simulated increasing the size of the big drops at the expense of the small drops as a function of time. However, as Binks *et al.* [43] had demonstrated employing N-dodecyl octaoxyethylene glycol, and mixed drops of squalene and decane in water, Ostwald ripening increases with the solubility of the oil. Thus, for heavy oil in water emulsions as those simulated in this paper, Ostwald ripening is not expected.

As previously stated, surfactant adsorption depends not only on time through surfactant diffusion, but it also depends on the total surfactant concentration, and on the spatial distribution of these molecules throughout the system. Surface saturation of all drops can only be achieved if there is enough surfactant to completely cover the available interfacial area. If the surfactant is homogeneously scattered throughout the system, it will distribute evenly between the available interfaces. If it is in-homogeneously distributed, those drops near the most concentrated zones will be covered first, and those drops far away from this region will get much less molecules or no molecules at all before some sort of "dynamic" equilibrium is established. Since the collisions between drops are on the same time scale of the surfactant diffusion, different surfactant distributions and/or concentrations will produce distinct DSD.

If surfactant adsorption is extremely fast, the effects of surfactant diffusion on coalescence are negligible. This is also the case of small oil/water volume-fraction-percentage ($\phi_{\mathrm{oil/water}}$) emulsions, even if surfactant adsorption is not very fast. Minimum collision times of: 11.9, 1.70 and 0.0017 seconds were found for 64, 125 and 216-particle calculations, departing from simple cubic arrangements (a = 3.9-μm, $D = 5.6 \times 10^{-14}\,\mathrm{m^2/s}$, $\phi_{\mathrm{oil/water}} =$ 15%, 30% and 51%, respectively). Slightly smaller times are expected for initial random arrangements which are only possible for the low volume fractions, since $\phi_{\text{oil/water}} = 52\%$ already corresponds to maximum packing for spheres of equal size distributed in simple cubic fashion.

The possible ways in which a surfactant can be initially partitioned throughout the system are almost as large as the number of degrees of freedom of the system. Roughly speaking, the surfactant can be homogeneously (H) or in-homogeneously (I) distributed. These situations are incorporated in the current version of the program through several distribution "strategies". These strategies can be sub-classified according to the quickness of the surfactant adsorption process. If the initial condition corresponds to a homogeneous (H) surfactant distribution, the surfactant adsorption can be fast (H-FA) or slow (H-SA). Besides, the adsorption can either be irreversible (H-FA1; H-SA1) or reversible (H-FA2; H-SA2). A similar classification can be formulated for inhomogeneous (I) surfactant distributions (I-FAl, *etc.*). Some possible realizations of these processes, for homogeneous distributions are:

(1) H-FA1: the surfactant distributes evenly among all drops, in a quick and irreversible way. Whenever the surfactant is very insoluble in the oil phase and its total concentration (c) is below the value necessary to stabilize the initial DSD ($c < c_c$; where subscript "c" stands for critical), this can be simulated ascribing to each drop a fraction of available surfactant. That fraction corresponds to the quotient between the area of the drop and the total available interfacial area: $N_k = N_{\text{surf}} * A_k / \sum A_i$ (where N_k is the number of surfactant molecules adsorbed to the interface of drop "k" of area A_k, and N_{surf} is the total number of surfactant molecules in the system). In the presence of an excess amount of surfactants all interfaces will be saturated and $N_k = A_k / A_{\text{surf}}$, where A_{surf} is the close-packed surfactant area.

(2) H-FA2: Similar to H-FA1, but instead of choosing the drops sequentially for surfactant distribution, they are randomly chosen at each step of the simulation. Thus, for $c < c_c$ the amount of surfactant at the surface of each drop changes with time, simulating a desorption/re-adsorption process.

(3) H-SA1: Slow adsorption occurs. This means that the number of surfactant molecules at the interface progressively increases with time. In this case A_{surf} is not constant, and it is given by Eq. (9) or a modification of it (Eqs. (10)–(12)). For $c > c_c$, $N_k = A_k / A_{\text{surf}}(t)$. For $c < c_c$, the number of surfactants is supposed to be homogeneously distributed among drops: $N_k = N_{\text{surf}} * (A_k / \sum A_i)$.

(4) H-SA2: Similar to H-SA1, but in this case the drops are chosen randomly for surfactant distribution purposes. Note that H-SA1 and H-SA2 only differ for $c < c_c$, in which case, there is not enough surfactant to cover all drops. Thus the surfactant population adsorbed at the interface of each drop changes with time not only due to the time dependency of A_{surf}, but also due to the random selection of the drops.

Similar techniques can be employed for simulating inhomogeneous surfactant distributions. The present calculations correspond to the I-FA1, H-FA1 and H-SA1 cases. In the I-FA1 it is assumed that a surfactant concentration gradient persists during the whole simulation. This gradient is likely to exist whenever the surfactant is only slightly soluble in the external (water) phase, or the time of stirring has been insufficient to distribute it evenly throughout the system. Since ionic surfactants are solid, we assume that the gradient decreases from the lower left-hand side corner of the simulation cell, to the diagonally opposite upper corner. In practical terms, this means that the drops are sequentially covered by surfactant, starting with those located at the bottom of the simulation cell and moving up from left to right. Some additional results corresponding to different realizations of the I-FA1 case will be also shown.

Once the surfactant is distributed between the available drops, the total charge and the surface potential of the drops can be computed. The diffusion constant of the drops is either introduced as input or estimated according to Stokes law. In either case, when the radius of the drop changes due to coalescence, its diffusion constant is re-evaluated employing an inverse dependence on the radius as predicted by Stokes. Following, the total force acting upon each particle is computed, and the particles moved in a Brownian Dynamics way (Eq. (1)). At each step, the program checks for overlap, in which case, a new particle is formed at the center of mass of the colliding drops, evaluating the new radius from a mass balance. A new diffusion constant is then calculated, and the available surfactant redistributed according to the previously selected scheme. At that time, the program re-computes the forces, and is ready for another iteration.

3. COMPUTATIONAL DETAILS

The input data required for these calculations includes: (a) the surfactant charge per molecule; (b) the ionic strength; (c) the diffusion constant of the initial drops; (d) the effective Hammaker constant; (e) the initial particle radii; and (f) the surfactant interfacial area at maximum packing. The present results correspond to the bitumen in water emulsion "E3" reported by Salou *et al.* [36]. The referred emulsion has an average drop radius of 3.9 μm, a very high ionic strength ($\kappa a = 1536$), a experimentally determined Hammaker constant of 1.24×10^{-19} Joules, and an electrostatic ζ-potential of +115 mV at pH = 2.9. Use of Eq. (7), allows calculation of the surfactant charge density that gives +115 mV for a drop of radius 3.9 μm at maximum surfactant coverage.

As shown by the extensive compilation of Rosen [44], the surfactant interfacial areas at water/air and water/oil interfaces, usually range from 30 − 70 Å^2. These areas depend on the nature of the oil phase, the ionic force of the dispersing phase, the chemical structure of the polar head, *etc.* Since the average interfacial area of natural amines at the Bitumen/water interface is unknown, it had to be estimated. For cationic surfactants (as those employed by Salou's *et al.*), some typical interfacial areas are: 38 Å^2 for Dodecyl trimethyl amonium chloride at air/water interfaces in 0.1 M NaCl solutions [45]; 48 Å^2 for tetradecyl pyridinium bromides in 0.5 M sodium bromide solutions, and, 64 Å^2 for tripropyl tetradecyl amonium bromide in 0.5 KBr solutions [46]. The maximum amount of surfactant in a drop of 3.9-μm was estimated supposing an average interfacial area of 50 Å^2 ($= A_{surf}$).

Three-dimensional periodic boundary conditions were employed under the minimum image convention. The initial configuration consisted in simple cubic arrangements of 64, 125 and 216 particles of equal radius ($\phi_{oil/water} = 0.15$, 0.30 and 0.51, respectively). The time step in units of (a^2/D) was set to 5×10^{-9} ($a = 3.9\,\mu m$, $D = 5.6 \times 10^{-14} m^2/s$), which for 150 million iterations corresponded to 3.49 minutes of real time.

The total surfactant concentration (c) ranged from 1.0×10^{-6} M to 1.3×10^{-3} M. In Type I (I-FA1) simulations, we supposed the existence of the referred surfactant concentration gradient. In Type II simulations a homogeneous surfactant distribution (H-FA2) between 216 particles was supposed. In this case, the surfactant was randomly distributed among drops at each step of the simulation. An additional 216-particle simulation with a gradient similar to that of Type I calculations, but with a volume fraction of oil of 0.30 was employed, distributed among 112 particles of 3.90 μm, and 104 particles of 1.95 μm, is identified as Type III. In Type IV computations the surfactant molecules were evenly distributed among all drops of the system according to the H-FA1 scheme described in Section II. Finally, one homogeneous calculation with time-dependent surfactant adsorption (H-SA1) was also computed. In this case, Eq. (9) was used to mimic surfactant adsorption, with t_0 and t_f values of 1.36 and 67.9 seconds (1 and 50 million iterations, respectively).

4. RESULTS AND DISCUSSION

As found in previous simulations [47] the dependence of the number of particles with time shows three distinct regions of variation. Region A ranges from $t^* = 0$ to the minimum time required for the first collision ($t^* = t_m$). If the surfactant concentration is not high enough to generate appreciable barriers towards coalescence between all drops, the number of particles will decrease with time (region B), lowering the available interfacial area until the remaining population can be suitably stabilized by the available surfactant molecules. Once that "critical" concentration (c_c) is reached ($t = t_c$), the number of particles remains constant (region C) unless some other destabilizing mechanism takes place (Ostwald ripening, phase inversion, sedimentation or creaming). This behavior has been already observed [48]. Cornell *et al.* [48] carried out a direct microscopic study on the motion of spherical polystyrene particles of 3.76 μm, at NaCl concentrations between 10^{-1} and 10^{-5} M. At the most dilute electrolyte concentration (high ionic strength) no change was observed in the number of single particles until 6.3 hours. Between 10^{-3} and 10^{-2} M the percentage of single particles initially decreased and then became constant over an extended period of time suggesting the possibility of a steady-state condition in the aggregation process. At higher electrolyte concentration (lower surface potential), the initial rate of disappearance increased. About critical coagulation concentration (very low ϕ_P), aggregation became very extensive after only 30 minutes.

Two different kinds of Region-B behavior were found (see Figs. 2–4). For the lower surfactant concentrations a monotonic decrease in the number of particles with time was observed, while for intermediate concentrations regions of rapid variation of the number of drops with time were observed.

Figure 5(a) shows the best fits of three of the most well known analytical equations for the 64-particle case at 1×10^{-6} M surfactant concentration (Type I). Smoluchowski's treatment [3] assumes that the flocculation rate is determined by diffusion, and the particles do not interact until contact, where irreversible flocculation occurs. Van den Temple expression [4] extends Smoluchowski's development to include the kinetics of coalescence, assuming that the coalescence rate is proportional to the number of contacts

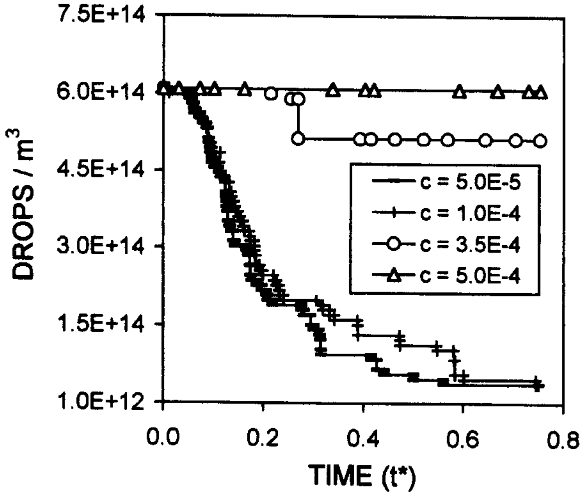

FIGURE 2 Particle concentration as a function of scaled time for an initial system of sixty four drops under the I-FA1 condition (Type I simulations). The total surfactant concentration is specified in the legend with letter "c". Time t* is in units of a^2/D.

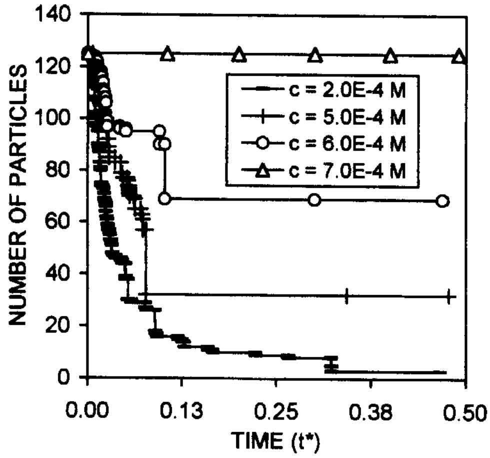

FIGURE 3 Variation of the number of drops with time for an initial system of one hundred twenty five 3.9-μm particles (Type I simulations).

between the particles. Borwakar *et al.*, development is a series expression on the constants of flocculation and coalescence based on a correction of van den Temple's work.

Since the referred theoretical formalisms do not account for the generation of a repulsive barrier of stabilization, we have fitted those

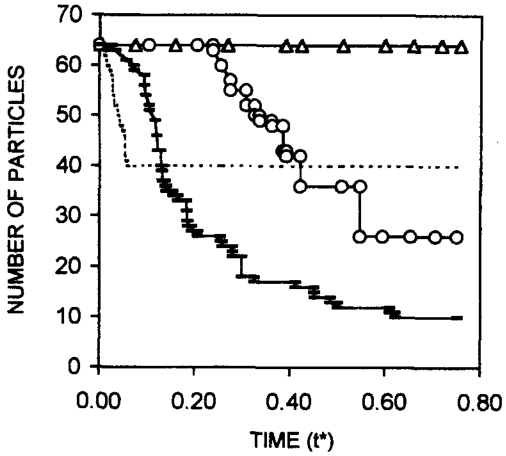

FIGURE 4 Number of drops as a function of time for Type IV simulations, at different surfactant concentrations: – 1.0×10^{-6} M; ○ 2.0×10^{-6} M; △ 1.0×10^{-4} M. The result of the Type-V simulation for $c = 1.0 \times 10^{-4}$ M (– – –) is also shown.

equations to the lowest surfactant concentration of both 64 and 125-particle simulations (Figs. 5(a) and (b)). First, the theoretical flocculation rate of Smoluchowski [3] was employed ($k_f = 4kT/\eta = 5.49 \times 10^{-18}\,m^3/s$) in all equations. Following, the flocculation and coalescence rate constants of each model were fitted until a minimum average difference between the simulation data and each theoretical prediction was obtained. As expected, the theoretical flocculation constant provided by Smoluchowski, produced the largest deviation. Fitted flocculation rates where typically one order of magnitude higher than k_f. For $c = 1 \times 10^{-6}$ M, the surfactant concentration is too low to generate a barrier towards coalescence, and fast flocculation should be anticipated. In Brownian Dynamics simulations of hard-sphere poly-ion particles immersed in a solution of counter-ions, by-ions, and a uniform liquid solvent [51], a significant increase of the effective diffusion constant was found. For $c = 1 \times 10^{-6}$ M, a totally attractive potential exists. Values ranged from 1 to 2 orders of magnitudes higher than Smoluchowski's prediction, depending on conditions and analytical equation employed.

Direct application of Fuchs' correction ($k' = k_f/W$) [49], employing Reering and Overbeek's stability factor ($W = k_f/2 * \exp(G_{max}/kT)$) [50] was not possible since the magnitude of the maximum free energy barrier between drops (G_{max}) continuously changed during the dynamics, as a consequence of unequal surfactant distribution among drops. Thus, both fast and slow flocculation took place between different drops at the same time as is supposed to happen in the experiment. Average W values

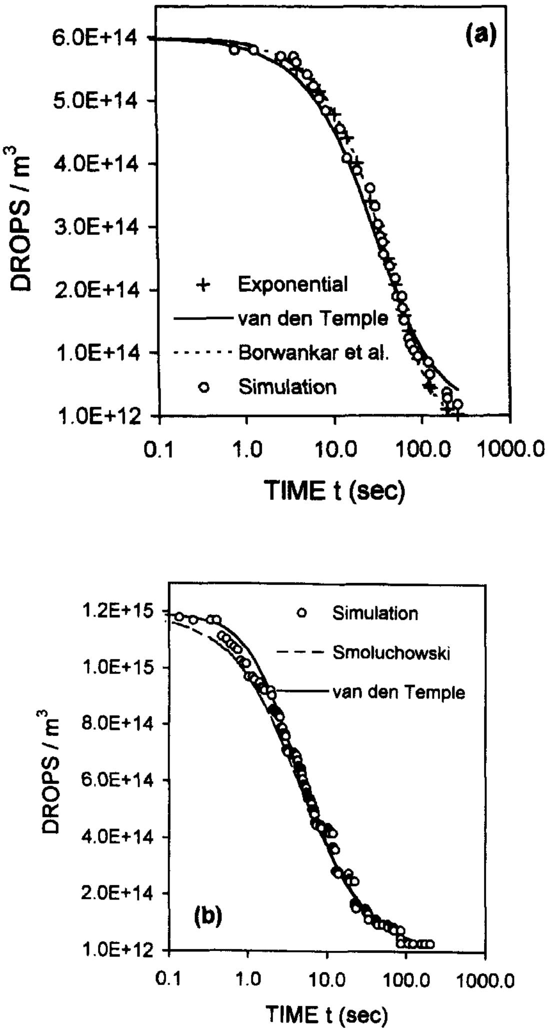

FIGURE 5 Comparison between the prediction of analytical theories [3–5] and the results of the simulation for: (a) a 64-particle Type-I calculation at a surfactant concentration of 1×10^{-6} M; (b) a 125-particle Type-I simulation at a surfactant concentration of 2×10^{-4} M. A logarithmic time scale had been used, for a better appreciation of the theoretical predictions.

calculated from the fitted flocculation constants ranged from 33 to 36 kT, for both 125 and 64 particle simulations at their lowest surfactant concentration.

For the 64-particle simulations ($\phi_{\text{oil/water}} = 15\%$) average deviations of 1.12, 1.13, 1.48 and 1.78 particles were found with respect to the theoretical formulae of Borwankar *et al.* [5], a simple exponential decay (e^{-Kt}), Smoluchowski's equation [3], and van den Temple's expression [4]. For the cases of Borwankar and van den Temple, the best results were obtained assuming that the number of contacts of a drop in an aggregate was equal or higher that the number of drops in that floc (m). As discussed by van den Temple, this assumption was expected to hold in concentrated emulsions, while an $m-1$ dependence is likely to be found in more diluted systems. Whenever this assumption holds and the coalescence rate is very high, the resulting van den Temple's equation reduces to Smoluchowski's formula for the number of primary particles per unit volume (n_1) that have not combined into aggregates ($n_1 = n_0/(1 + k_f n_0 t)^2$; n_0 being the initial number of particles per unit volume). Thus, van den Temple and Smoluchowsky-n_1 curve (not shown) look similar. As shown by Danov *et al.* [52], Smoluchowsky's n_1 expression also holds for the number of "single" particles whether they resulted from coagulation or had not collided at all. Borwankar *et al.*, series expression [5] was kept up to fourth order, but under the present calculation conditions, no significant error was found when all terms except the first were eliminated. That term is a simple exponential decay ($K = 0.0205\,\mathrm{sec}^{-1}$) also shown in Figure 5(a). As in the case of van den Temple's formula, the greatest deviations occur at long times, when the simulation predicts the attainment of a steady state. It should be noticed that for 64-particle simulations an average deviation between 1 and 2 particles is fairly high. However, both van den Temple and Borwankar *et al.*, model can be fitted to a good degree of accuracy for small and intermediate times ($t < 60$ sec). For longer times, a slow decrease in the number of particles is predicted by the analytical formulae, while a constant number of particles is suggested by the simulations in the absence of Ostwald ripening (as occurs for similar drop-sizes and negligible oil solubility).

Interestingly, the $\phi_{\mathrm{oil/water}} = 30\%$ (125-particle) calculations appear to be more accurately described by van den Temple and Smoluchowski treatments, than by Borwankar *et al.*, equation. Average deviations of 1.21, 1.39 and 4.95 particles were found for these cases, respectively. The half life period of the less stable emulsions ranged from 4.5 to 8.7 seconds for the $\phi_{\mathrm{oil/water}} = 30\%$ dispersions, and from 27.7 to 33.8 seconds for the $\phi_{\mathrm{oil/water}} = 15\%$ emulsions.

According to our simulations, the critical surfactant concentration is not a fixed number for a given Drop Size Distribution (DSD), but depends on surfactant partitioning. If a surfactant concentration gradient exists and local equilibrium is assumed, some drops will be covered by surfactant after emulsification while other will not. In this case the amount of surfactant necessary to generate a repulsive barrier between all drops must be relatively "high", since the surfactants are likely to cover all accessible areas up to saturation, in the most concentrated zones. In this case, the number of surfactant molecules (N_{surf}) required to stabilize a given DSD is approximately equal to the quotient between the total interfacial area (ΣA_i; where A_i is the area of each drop) and the surfactant area, A_{surf}. On the other hand, if the surfactant molecules are evenly distributed throughout the system (Fig. 4), maximum adsorption is not required to prevent coalescence, and a much lower surfactant concentration might be sufficient to generate a minimum repulsive barrier among all particles ($A_c \ll N_{surf}A_{surf}$). Thus, a surfactant concentration of 1×10^{-4} M is enough to stabilize a 64-particle system under Type-IV conditions (see Fig. 4), but not enough to stabilize the same system in the presence of surfactant concentration gradient (see Fig. 2). According to our simulations, the surfactant concentration required for the complete stabilization of a $\phi_{oil/water} = 15\%$ emulsion under a homogeneous surfactant distribution, can be up to two orders of magnitude lower, than the one required for the inhomogeneous case.

The Type-V simulation is also shown in Figure 4. For this simulation a total surfactant concentration of 1×10^{-4} M was also employed. As expected, the final number of drops (40) is intermediate between those of Type IV (64) and Type I (4) calculations. The number of surviving drops depends on how many collisions occur before a substantial amount of surfactant can reach the interfaces of the drops. Thus, even if the total surfactant concentration used is in principle high enough to stabilize the initial drop size distribution, the stable DSD is a decreasing function of the surfactant adsorption time.

Figure 6 shows the sizes and XY-positions of the drops at the end of the simulation for the 125-particle systems. Due to the high ionic-strength of the liquid medium, the secondary minimum is located very close to the surface. Thus, it is observed that the surviving particles clump together in certain regions of the simulation box.

Figure 7 shows the variation of the "steady-state" interfacial area (A_c) in terms of the surfactant concentration (c). In Type I simulations of 64, 125 and 216 particles, the number of drops show a concentration-dependence similar to that of a step-function. At very small surfactant concentrations, all drops are destabilized until they coalesce into a single particle. Lower concentrations will not decrease A_c further. At very high surfactant concentrations all drops in the initial DSD are completely covered by surfactant. In this case, the DSD remain constant with time since for $c = c_c$ the surface potential of each drop is the highest possible (+115 mV for

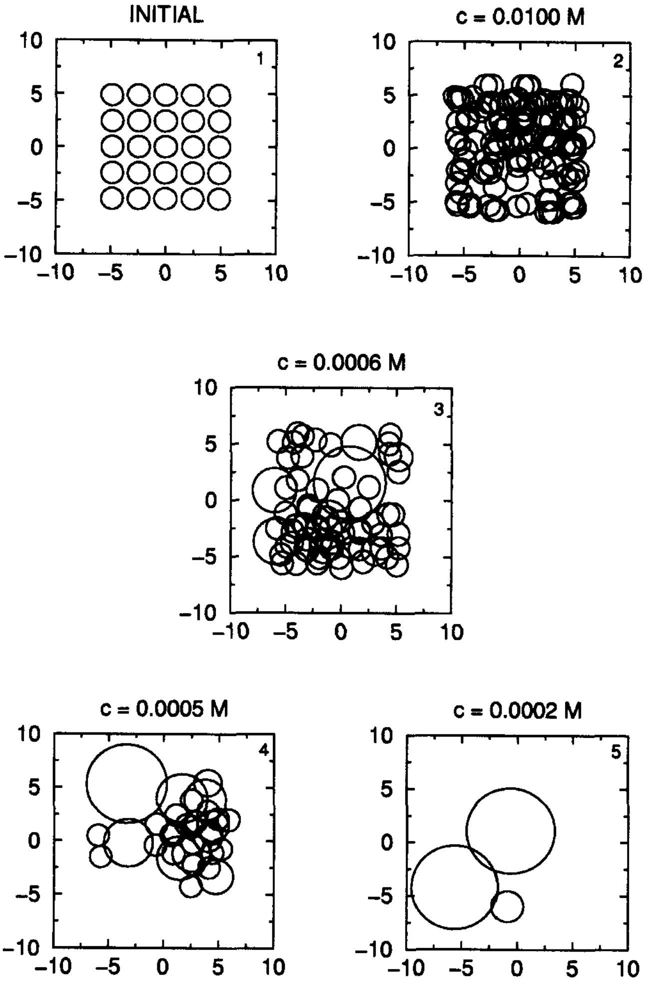

FIGURE 6 Final XY coordinates of the remaining drops at the end of the simulation for an initial 125-particle system. The original configuration is illustrated in inset "1".

3.9 μm drops). Higher surfactant concentrations (within the two-phase region) do not produce an enlargement of A_C. In between those two extremes, A_c increases monotonically with c. All simulations appear to follow a similar pattern but the complete data does not merge into a single curve, mostly because the surfactant concentrations required to stabilize 64, 125 and 216 particles of equal radius are different.

As expected, Type I and II simulations with the same number of particles show noticeable differences except at their end points (Fig. 7).

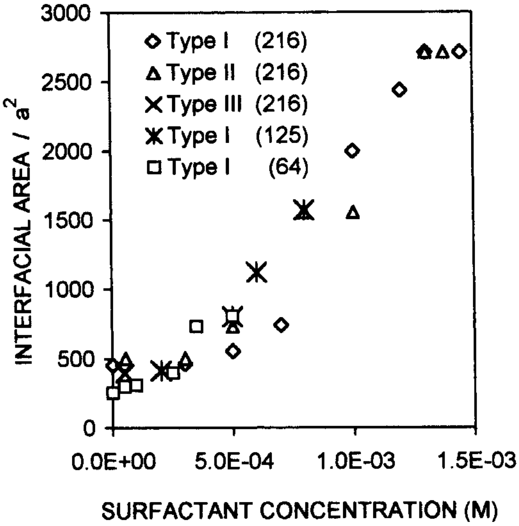

FIGURE 7 Total interfacial area of the stable emulsions as a function of surfactant concentration. Simulations were carried out with 216, 125 and 64 drops, and different surfactant distribution mechanisms (see text).

These differences are caused by the mechanism of surfactant distribution. Unpublished results on Type IV simulations show that the overall appearance of the interfacial area/concentration curve is very similar to Figure 7, but shifted towards much lower surfactant concentration. It was already shown that a surfactant concentration of 1.0×10^{-4} M is enough to stabilize 64 drops, whenever the surfactant is homogeneously distributed throughout the system. These H-FA1 results are consistent with Salou *et al.*, data [36], who found that stable bitumen emulsions are obtained for high resin/asphalthene ratios, and surface potentials of 50 mV. For Type IV simulations, a surfactant concentration of 1.0×10^{-4} M produces a surface potential of $\phi_p = 50.7$ mV in all drops. According to Verwey and Overbeek [26], coalescence is feasible whenever the DLVO barrier is lower than 25 kT. For a homogeneous surfactant distribution, this barrier is obtained whenever $c = 8.1 \times 10^{-5}$ M, $\phi_p = 44.3$ mV, a surface potential still close to Salou *et al.*, findings.

5. CONCLUSIONS

A new technique for studying the influence of surfactant adsorption on emulsion stability towards flocculation and coalescence was described. It had been used to simulate the effects of surfactant distribution in the elaboration of highly concentrated bitumen in water emulsions stabilized by natural cationic surfactants. The drops were assumed to interact through a DLVO potential, whose electrostatic contribution changed with the number of surfactant molecules at the interface. These preliminary results showed the influence of the mechanism of surfactant adsorption on the emulsion stability. In the present case, a steady state conditions in the variation of the DSD with time is achieved by the generation of a electrostatic surface potential of at least 44.3 mV.

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