

## Surface Chemistry and Gas Hydrates in Flow Assurance

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A review of surface chemistry concepts is presented, with the principal objective of identifying interfacial phenomena and surface chemistry interactions involved in gas hydrate formation and agglomeration in oil and gas pipelines. There are five types of interfaces where gas hydrates may form and aggregate: gas/liquid, liquid/liquid, gas/solid, liquid/solid, and solid/solid; where the gas is the hydrocarbon gas, liquid is either oil, water, or condensate, and solid is either gas hydrate or the pipe wall surface. A review of fundamental interfacial concepts can help create a better understanding of phenomena at these interfaces, and can help industry move from hydrate prevention to risk management. Two areas of surface chemistry have been selected to illustrate the concepts and mechanisms associated with these systems: surfactants and emulsions. Examples from the literature pertaining to gas hydrates are presented for each system.

### Introduction

The oil and gas industry is moving toward more challenging scenarios with offshore explorations in deeper and colder waters. The production facilities will require longer subsea tiebacks for the transport of hydrocarbons from the wellhead to the production/processing platforms, and may require the transportation of processed gas/condensate streams to export facilities through subsea pipelines.

The flow assurance of the produced hydrocarbon stream is a critical technical concern that focuses on the design of safe and secure operation techniques for the uninterrupted transport of reservoir fluids from the reservoir to the point of sale. The formation of solid deposits of gas hydrates, waxes, asphaltenes, and scale that plug the pipelines represents one of the principal problems in flow assurance. Because of their rapid formation gas hydrates are considered by far the most serious and common problem in flow assurance in the case of deep subsea transportation compared to other solid deposits.<sup>1</sup>

Gas hydrates are crystalline compounds formed by the hydrogen-bonded water molecules in a lattice structure that is stabilized by encapsulating a small guest molecule, such as methane or ethane.<sup>2</sup> Hydrates form in the presence of appropriate quantities of gas and water molecules, typically at high pressures and low temperatures. The interface between water and gas phases represents an ideal location for the formation of gas hydrates in hydrocarbon production systems.

Figure 1 illustrates a proposed model for hydrate formation in a multiphase flow system containing water, oil, and gas,<sup>3</sup> where hydrates form at the interface of water droplets entrained in the oil phase, and/or from gas bubbles entrained in the water phase. Frequently as little as 4 vol% of the water is formed into hydrate, when a plug occurs.<sup>4</sup> In the oil phase, these hydrate-encrusted water droplets can agglomerate into larger hydrate masses, leading to an increase in the slurry viscosity, which can eventually form a plug. The surface of water droplets in water-in-oil (W/O) emulsions is a critical location for the formation and agglomeration of hydrates. Another aspect that calls the attention of industry and academia are the so-called

naturally inhibited oils,<sup>5</sup> which are characterized by having natural surfactants that seem to prevent the agglomeration of hydrate particles and allow the transport of hydrate slurries without the formation of plugs.

Motivated by the above observations, this work focuses on a review of fundamental concepts of surfactants and emulsions, two main subjects of surface chemistry, identifying interfacial phenomena and surface chemistry interactions involved in gas hydrate formation and agglomeration in oil and gas systems. The concepts and current understanding presented form the basis for the development of novel techniques for the prevention and remediation of gas hydrates.

### Surfactants

The presence of natural surfactants (acids/salts, alcohols, ethers, esters, and other organic compounds) in oil systems and synthetic surfactants (corrosion inhibitors, hydrate antiagglomerants and kinetic inhibitors, demulsifiers, antifoaming agents, etc.) introduced into the phases of the production stream motivate considerations of surfactants in this review. Surfactants are amphiphilic molecules which exhibit a double affinity for polar and nonpolar substances. In its simplest configuration, a surfactant molecule has two types of functional groups, a hydrophilic or polar group (water-soluble), and a lipophilic or nonpolar group (oil-soluble) which is generally a hydrocarbon chain with at least 12 carbon atoms; one example of a common surfactant is sodium dodecyl sulfate (SDS) and a schematic of a typical molecular structure is illustrated in Figure 2.

The balance of effects produced by the type, size, and strength of the hydrophilic and lipophilic groups will determine the properties of the surfactant molecule. The surfactant molecule will tend to be water-soluble if the hydrophilic group is more important, in particular if the surfactant is ionized and the lipophilic hydrocarbon chain is relatively short (e.g., <12 carbon atoms in length). On the other hand, a long hydrocarbon chain (e.g., >16 carbon atoms) will make the surfactant molecule more oil soluble. The surfactant chemical structure and other parameters depending on the different fluids, temperature, and pressure can alter the affinity of surfactants with the water and oil phases, as will be discussed later.

Surfactant molecules present two fundamental properties: interfacial adsorption and self-association, which are the essential

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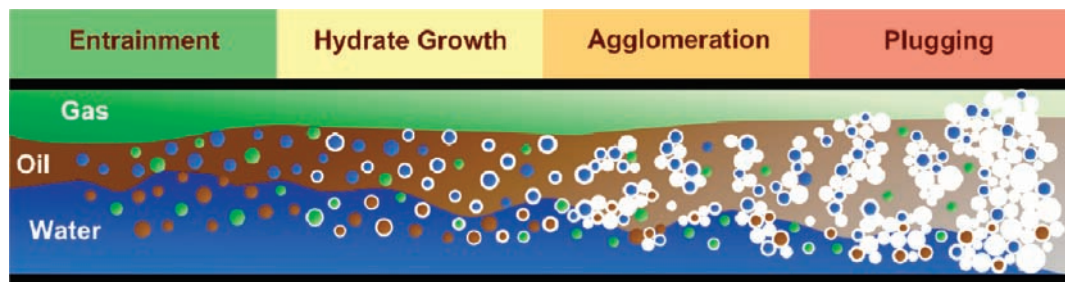


Figure 1. Conceptual model for hydrate formation in a multiphase flow systems consisting of water, oil, and gas (adapted from ref 4).

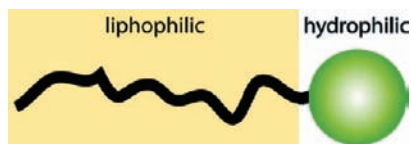


Figure 2. Schematic of a surfactant molecule, identifying hydrophilic and lipophilic groups.

processes leading to surfactants forming structures and enhancing solubilization. The adsorption of surfactant molecules to interfaces is driven by its double affinity to polar and nonpolar substances, where a minimum in free energy of the system is attained. The surfactant can diffuse from a bulk phase to an interface, such as gas/liquid, liquid/liquid, and liquid/solid interface, decreasing the surface or interfacial tension, modifying the contact angle between the phases and wettability of solid surfaces, and changing surface charge and surface viscosity.<sup>6</sup> The surfactant adsorption onto solid surfaces depends on the original wettability of the solid: if the solid is oil-wet, the surfactant adsorbs from the lipophilic tail, and if it is water-wet, the surfactant adsorbs from the hydrophilic head. The intrinsic wettability depends on the nature of the solid and liquid substances, particularly their polarity. However, this a complex matter because the wettability is a property that is not always at equilibrium and may exhibit hysteresis phenomena that vary with the history on contact of the liquid with the surface. Some schematic diagrams of the adsorption of a surfactant molecule to interfaces are shown in Figure 3.

Initially, when water-soluble surfactants are added to an aqueous solution phase, surfactant molecules adsorb to any available interface until the interface is saturated. The orientation and the structure depend on the system (see Figure 3), in particular with respect to the electric charges on the surface, which can produce a single or double layer adsorption depending on the charge present at the solid interface, and consequently result in a hydrophobic or hydrophilic adsorbed layer. With increasing surfactant concentration, surfactant molecules start to associate, forming spherical aggregates called micelles. The surfactant association is driven by the hydrophobicity of its lipophilic group which avoids mixing with water. The surfactant concentration at which the first micelle is formed is known as the critical micelle concentration (CMC), and may be detected from a discontinuity in the change of several variables such as surface tension, osmotic pressure, viscosity, electrical conductivity, and density.<sup>7</sup> Figure 4 shows a typical plot of surface tension and electrical conductivity as a function of surfactant concentration, indicating the discontinuity of these properties at the CMC.

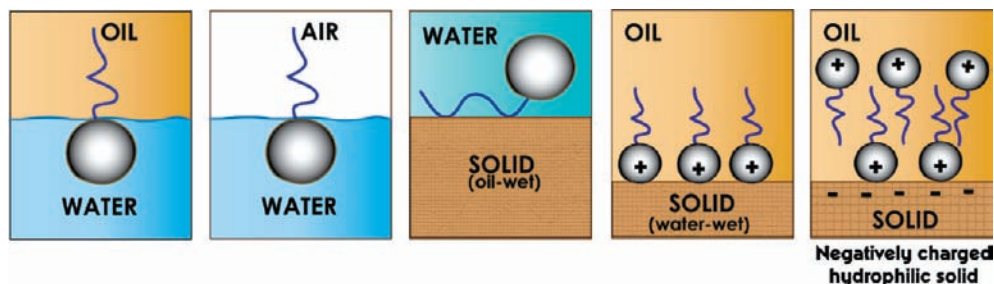
The CMC depends upon the surfactant molecular structure and physicochemical conditions (i.e., temperature, pH, ion concentration). Above the CMC, additional surfactant molecules incorporate into micelles, while the concentration of unassociated single surfactant molecules (monomers) remains nearly

constant in a dynamic equilibrium between monomers and micelles, with constant swapping of molecules between micelles and the bulk phase. A further increase in surfactant concentration can promote the formation of more complex aggregates in the form of cylindrical, hexagonal-packed, lamellar structures, worm like micelles, vesicles, liposomes, and other structures.<sup>6</sup> Inverse micelles are formed in oil-soluble surfactants when the hydrophilic part aggregates to avoid mixing with the oleic (oil) phase. Figure 5 shows a schematic of normal and inverse micelles.

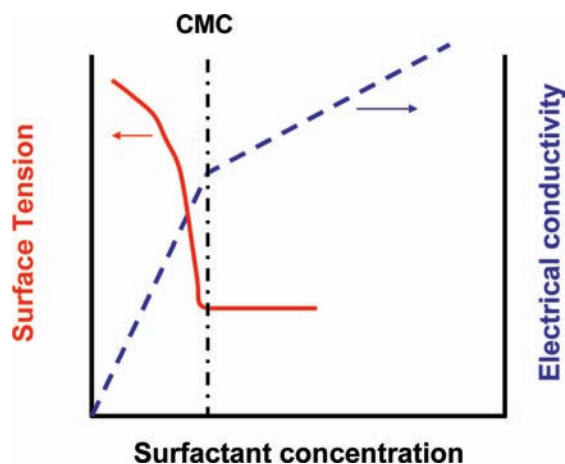
Another important property of surfactant solutions is the solubilization of nonpolar molecules (oil) inside normal micelles in the aqueous phase or water inside inverse micelles in the oleic phase. Above the CMC, the solubilization increases by incorporation of a nonsoluble phase inside the micelles. When the formulation of the solution is close to the hydrophilic–lipophilic balance of the surfactant with both oil and water phases, a microemulsion phase can be formed. Bicontinuous microemulsions are typically defined as containing normal and inverse swollen micelles (filled with oil and water), which are combined to result in a single phase structure,<sup>8–10</sup> as shown schematically in Figure 6, where a close to zero curvature of a surfactant layer is limiting the oil and water zones.

**Effects of Surfactants in Gas Hydrate Formation.** The association of surfactant molecules in the form of micelles at concentrations above the CMC accelerates gas hydrate formation and reduces the induction time in quiescent systems, which is of special interest for the application of gas hydrates in the storage and transportation of natural gas.<sup>11</sup> Zhong and Rogers<sup>12</sup> studied the effect of SDS on the hydrate formation mechanism using ethane and natural gas as guest molecules. They suggested that micelles act as a nucleation point by increasing the solubility of hydrocarbon gas in the aqueous phase and by inducing the formation of hydrate crystals around the micelle in the bulk water phase below the gas/water interface. Consequently, the hydrate formation rate was observed to increase by more than 700 times and the induction time for nucleation decreased compared to systems without surfactant. Other studies had obtained similar effects with different surfactants, but invoked a different mechanistic explanation,<sup>13,14</sup> questioning the CMC formation requirement.

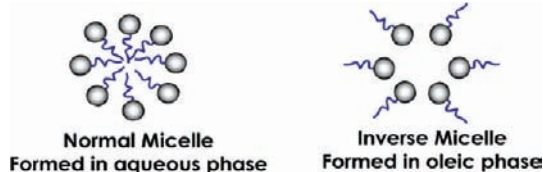
The morphology of the hydrate film that forms at hydrocarbon/water interfaces is affected by the adsorption of surfactant molecules at the interface. Luo et al.<sup>15</sup> studied gas hydrate formation in a methane bubble column without surfactants, observing the formation of a hydrate shell around gas bubbles, which hindered further formation of gas hydrates. The effect of SDS, below the CMC, on hydrate formation on gas bubbles using a static mixer was studied by Tajima et al.,<sup>16</sup> who reported an increase in hydrate formation rate and a change in the morphology of the hydrate film with the addition of SDS. The adsorption of surfactant at the bubble interface promoted the formation of a rougher hydrate film with a weaker structure



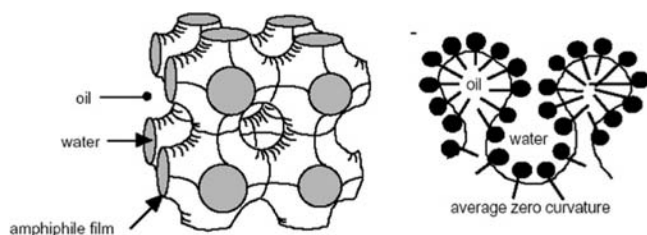
**Figure 3.** Adsorption of a surfactant molecule at the liquid/liquid, gas/liquid, and liquid/solid interfaces (with two typical cases related to the solid surface electrical charge).



**Figure 4.** Variation of surface tension and electrical conductivity as a function of surfactant concentration, indicating the discontinuity at the CMC.



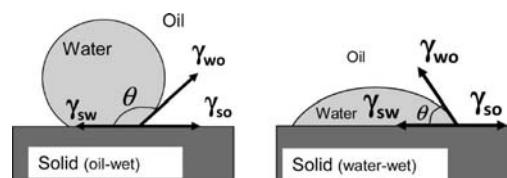
**Figure 5.** Association of surfactant molecules forming normal micelles in an aqueous phase and inverse micelles in an oleic (oil) phase.



**Figure 6.** Bicontinuous structure of microemulsions formed by associating both types of micelles and resulting in a zero curvature surfactant film that separates oil and water zones (adapted from ref 5).

that easily collapsed; the increase in hydrate formation rate was attributed to higher mass transfer through the hydrate film and surface renewal by the film collapse.

In another study, Kalogerakis et al.<sup>11</sup> compared the effect of anionic and nonionic surfactants in a stirred cell, reporting a greater increase in methane hydrate formation rate with an anionic surfactant (SDS). From the experiments with anionic surfactant, aggregates of hydrate particles suspended in the liquid phase were observed, increasing the slurry viscosity. Hydrate growth on the reactor wall was attributed to a more water-wet wall due to the anionic surfactant solution. The effect of anionic surfactants seems to be detrimental for the transportability of



**Figure 7.** Balance of interfacial tensions among the three phases at contact point, indicating contact angle of the liquid with the solid surface (left: solid is oil-wet; right: solid is water-wet).

hydrate slurries and should be avoided in pipelines, while nonionic surfactants seem to prevent the agglomeration of hydrate particles.

These studies exemplify the changes in the interfacial properties between the gas and water phases caused by the presence of surfactants. Surfactants tend to promote the formation of hydrates at the interface by lowering the interfacial tension at the water/gas interface, thus facilitating the transport of gas in contact with water.

**Effect of Surfactants on Contact Angle, Wettability, and Adhesion Forces of Hydrate Particles.** The wettability of a solid surface by a liquid is determined by the contact angle,  $\theta$ , which a liquid drop makes with the surface at the three-phase contact point (see Figure 7). Young's equation (eq 1) represents the relationship of the balance of interfacial tensions between the three phases at the contact point with the contact angle,

$$\cos \theta = \frac{\gamma_{so} - \gamma_{sw}}{\gamma_{wo}} \quad (1)$$

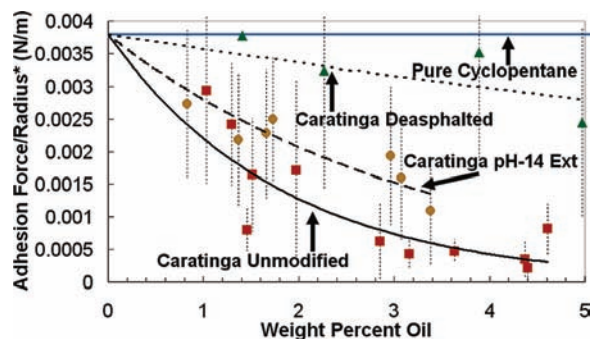
This equation shows the dependence of the contact angle on the nature of the liquids and the solid, i.e., interfacial tension of the liquid phases,  $\gamma_{wo}$ , and the solid free energies with the liquids,  $\gamma_{sw}$  and  $\gamma_{so}$ . A solid is water-wet if the water drop contact angle is lower than  $90^\circ$  and oil-wet if the contact angle is greater than  $120^\circ$ . For intermediate values of the contact angle, there is no preference for the liquid phase to wet the solid.

Young's equation is useful to determine the wetting equilibrium of a solid. However, the wettability can be determined thermodynamically using the spreading coefficient defined in terms of the interfacial tensions,<sup>17</sup>

$$S_{w/s} = \gamma_{so} - \gamma_{wo} - \gamma_{sw} \quad (2)$$

Spontaneous spreading of the water drop occurs when  $S_{w/s} > 0$ , i.e., decreasing the interfacial tension between water–oil and solid–water. The addition of a surfactant that decreases the interfacial tension between water–oil and solid–water can make the solid more water-wet. However, the actual wettability of the solid will depend on the nature of the surfactant.

It is often difficult to determine the wettability of hydrate surfaces, as a flat/smooth surface is required for measurements



**Figure 8.** Summary of adhesion forces between cyclopentane hydrates particles in the presence of Caratinga crude oil, measured by Dieker et al.<sup>20</sup>

of the contact angle. Høiland et al.<sup>18</sup> qualitatively studied the wettability of freon hydrates in water/oil emulsions by comparing the emulsion inversion point of different crude oils with and without hydrate particles, demonstrating that the wettability of hydrate particles depends on the oil composition. Oil-wet hydrate particles are attributed to the adsorption of natural surface active components of crude oils on the hydrate surface, which are correlated to have a low hydrate plugging risk in pipelines. Intermediate and water-wet hydrate particles are believed to contain less or none of these oil-wetting components, and are correlated to have a high hydrate plugging risk. Natural oil components that interact with hydrate surfaces are characterized to have polar functional groups and to be surface active, such as petroleum acids and bases.<sup>19</sup>

Aspenes et al.<sup>20</sup> studied the influence of oil composition on the wettability of pipeline surfaces, suggesting that the same natural components of oil that interact with hydrate surfaces also influence the pipeline surfaces. It was suggested that oils with high acids content compared to bases are more likely to form oil-wetting surfaces, resulting in lower hydrate plugging tendency.

The nonplugging hydrate tendency of systems with oil-wet hydrate particles and pipeline surfaces is supported by the work of Dieker et al.,<sup>21</sup> where micromechanical force measurements were used to quantify the adhesion forces between cyclopentane hydrate particles. An increase in the adhesive forces between hydrate particles was measured when the surface active components were removed from the crude oil. Figure 8 is a summary of the adhesion force measured by Dieker et al.<sup>21</sup> for the Caratinga crude oil, which is known to be a naturally inhibited, hydrate-transportable oil. From a SARA analysis<sup>22</sup> the Caratinga oil has an asphaltene content of 6.2%, saturates 39.8%, aromatics 39.8%, and resins 14.3%. Note the increase in adhesion force when the acidic components were extracted from the Caratinga oil (through a “pH-14 extraction” process), and a further increase in adhesion forces when the asphaltenes were extracted. The observed increase in adhesion forces correlates well with an increase in interfacial tension from its original value of 23 to 31 mN/m after the removal of acids, which implies that the absence of surface active compounds on the hydrate surface contributes to the increment on adhesion forces.<sup>22</sup>

Additional evidence that associates oil-wet surfaces with low hydrate plugging tendency is provided by the work of Aspenes et al.<sup>23</sup> who studied adhesion forces between cyclopentane hydrate particles and different solid surface materials. It was concluded that adhesion forces are higher for water-wet pipeline surfaces, which may be part of the mechanism for hydrate plug formation, and that addition of petroleum acids to the oil phase drastically reduces adhesion forces.

At this point the importance of the role of surfactants can be seen, with the surfactant fundamental property of interfacial adsorption, in the formation of gas hydrates at hydrocarbon/water interfaces and defining the wettability of hydrate particle and solid surfaces.

## Emulsions

In this section, a brief discussion of fundamental concepts and mechanisms of emulsions behavior will set the framework to understand the effect of emulsions on hydrate formation/dissociation and plugging formation tendency in pipelines.

In the petroleum industry, two types of emulsions are frequently encountered: water-in-oil (W/O) and oil-in-water (O/W) emulsions. Emulsions are defined as thermodynamically unstable mixtures of two immiscible liquids (one continuous and one dispersed), which means that they will separate over time. The separation of the immiscible phases will depend on the rate of coalescence of the dispersed phase. The stability of emulsions can be extended by kinetics means, making the separation time longer through complex interfacial mechanisms that delay the coalescence of the dispersed phase.

The formation of an emulsion requires at least three components: two immiscible phases (water and oil) and an emulsifying agent, which may be a natural component of one phase, or an emulsifying agent may be added to one of the phases. The emulsifying agent usually is a surfactant that adsorbs at the interface between the immiscible phases; some natural surface-active components in crude oils include asphaltenes, resins with organic acids and bases, naphthenic acids, and carboxylic acids, among many others.<sup>24–26</sup> Solid particles can also act as stabilizing agents, as in examples of sand, clays, mineral incrustations, corrosion products, paraffin wax, and precipitated asphaltenes.<sup>24,25,27</sup>

The rupture mechanism of an emulsion involves three basic steps: (i) long distance approach of dispersed drops by sedimentation and creaming, (ii) drainage of the thin film between drops, and (iii) coalescence of drops to become a single larger drop. The kinetic stability of an emulsion is attained by mechanisms that influence the thin film drainage. Four mechanisms have been listed as the principal mechanisms acting to stabilize emulsions: (1) the electric double layer, (2) the steric repulsion, (3) the Marangoni–Gibbs effect, and (4) the formation of a rigid cross-linked network adsorbed at the droplet interface.<sup>27,28</sup> A schematic representation of the emulsion stability mechanisms is presented in Figure 9.

The electric double layer represents the distribution of charges at the liquid–liquid interface caused by the adsorption of ionic surfactants. When two droplets come into contact, the charged surfaces repel each other preventing agglomeration and coalescence;<sup>29,30</sup> this mechanism plays a significant role in stabilizing O/W emulsions.<sup>28,30</sup> Steric repulsion prevents approaching droplets from coalescing due to physical barriers of adsorbed material such as polymer or surfactant chains.<sup>30</sup> The Marangoni–Gibbs effect describes the process whereby an expanding surface shows a subsequent decrease in surfactant concentration and increase in interfacial tension; the interfacial tension gradient generated provides the driving force for the flow of surfactant to areas of high tension, opposing film thinning.<sup>28,30</sup> The adsorption characteristics of the surfactant have a direct effect on the kinetics phenomena.<sup>31</sup> The formation of rigid cross-linked networks at droplet interfaces is associated with asphaltenes.<sup>28</sup> Even low amount of resins in the oil phase can improve the stability of emulsions by breaking up large asphaltene aggregates, which are then more mobile and hence

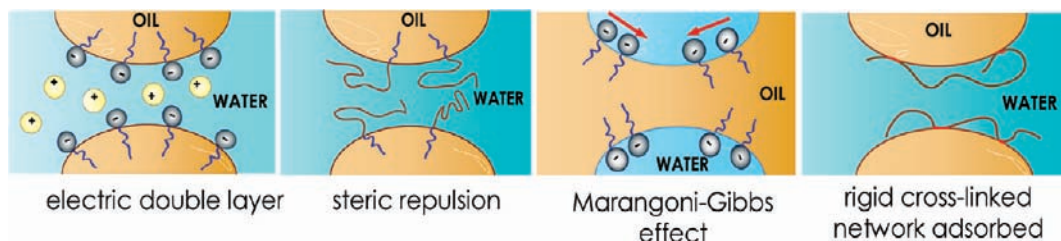


Figure 9. Mechanisms of emulsion stability (adapted from ref 24).

able to adhere at water–oil interfaces forming a strong interfacial network.<sup>32</sup>

Emulsion properties, such as emulsion type, droplet size distribution, stability, and rheology depend mostly on the following formulation variables: nature of the oil (equivalent alkane carbon number), salinity of the aqueous phase (type and concentration of electrolyte), nature and concentration of surfactant, and temperature. A general relationship may be established between the generalized formulation<sup>33</sup> and the trend variation, i.e., the increase or decrease of the different emulsion properties,<sup>34</sup> the intensity of which is influenced by the previous mechanisms. Other variables which influence emulsion properties are pressure, order of mixing, and energy input.

With the studies of surfactant–water–oil systems, different formulation approaches have been developed that can be used to predict or estimate the emulsions type and properties.<sup>35</sup> Developed from empirical observations, the Bancroft rule<sup>36</sup> states that the continuous phase will be the one in which the surfactant is most soluble. Another empirical method is the hydrophilic–lipophilic balance (HLB), which assigns a number to a surfactant based on its solubility in water.<sup>37</sup> Oil-soluble (lipophilic) surfactants have an HLB number lower than 9, whereas water-soluble (hydrophilic) surfactants have an HLB number greater than 11. A general rule-of-thumb is that a surfactant with an HLB ranging 4–6 will tend to form a water-in-oil (W/O) emulsion and an HLB ranging 8–18 will tend to form an oil-in-water (O/W) emulsion; this method correlates well with the Bancroft rule. These methods focus only on the nature of the surfactant and do not consider the effects of other formulation variables (e.g., temperature, salinity of water, oil phase composition).

A theoretical concept was introduced by Winsor<sup>38</sup> that relates the surfactant with its physicochemical environment at the interface between water and oil phases, describing three elementary types of phase behavior. The Winsor ratio ( $R = A_{CO}/A_{CW}$ ) is defined as the ratio of the net interaction energy of the surfactant with the oil phase ( $A_{CO}$ ) to the net interaction energy of the surfactant to the aqueous phase ( $A_{CW}$ ). When the interaction of the surfactant with the aqueous phase is greater than the interactions with the oil phase ( $R < 1$ ), a type I phase behavior results, consisting of a pure oil phase and an oil-in-water microemulsion phase with normal micelles of surfactant solubilizing oil; this type of system will tend to form an O/W emulsion. If the interaction of the surfactant with the oil phase is greater than that of water ( $R > 1$ ), a type II phase behavior is exhibited, consisting of a pure aqueous phase and a water-in-oil microemulsion phase with inverse micelles solubilizing water; this type of system will tend to form a W/O emulsion. The type III phase behavior corresponds to equal interactions of the surfactant with oil and aqueous phases ( $R = 1$ ), consisting of three phases in equilibrium: a microemulsion containing the surfactant which solubilizes large amounts of oil and water, and

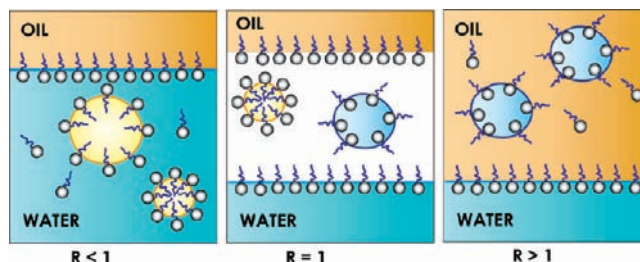


Figure 10. Schematic representation of phase behavior described by Winsor for different values of the ratio of net interaction energy of the surfactant with the oil phase to the net interaction energy of the surfactant to the aqueous phase.<sup>34</sup>

pure oil and pure water phases. A schematic representation of the three Winsor phase behavior types is presented in Figure 10.

A change in the formulation variables can promote a change in the interaction energies of the surfactant with the oil and aqueous phases, and therefore a change in the phase behavior. For example, an increase in the salinity concentration of the water phase would decrease the interaction energy of an anionic surfactant with the aqueous phase, thus promoting a change from type I to type III, and a further increase in the salinity will eventually lead to a type II phase behavior where all the surfactant molecules are in the oil phase. The Winsor  $R$  ratio can be used to make qualitative estimations of the changes in phase behavior, and ultimately in the emulsion type, when the formulation variables are modified.

The surfactant affinity difference (SAD) can be considered as a generalized formulation parameter that provides a quantitative approach of the relationship between the phase behavior described by Winsor and the formulation variables.<sup>39</sup> The concept of the effect of different formulation variables in a single expression was presented by Salager et al.<sup>40</sup> and Bourrel et al.,<sup>41</sup> and was then called surfactant affinity balance.<sup>42</sup> Using the definition of surfactant affinity deviation or difference as the negative of the chemical potential,  $SAD = \mu_w^o - \mu_o^o$ , where  $\mu_w^o$  and  $\mu_o^o$  are the standard chemical potentials of the surfactant in the water and oil phases, respectively. When the surfactant affinity for the water phase equals its affinity for the oil phase,  $SAD = 0$ , which is equivalent to a Winsor type III phase behavior ( $R = 1$ ). When  $SAD < 0$ , the affinity of the surfactant toward water dominates, forming O/W emulsions (Winsor type I). For  $SAD > 0$ , the affinity of the surfactant is stronger for the oil phase, forming W/O emulsions (Winsor type II). For ionic and nonionic (polyethoxylated) surfactants, the SAD expressions are as follows:

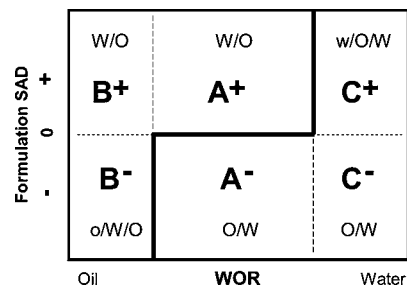
$$SAD/RT = \ln S - K[(E)ACN] - f(A) + \sigma - a_T(T - T_{ref}) \quad (3)$$

$$\text{SAD}/RT = bS - K[(E)\text{ACN}] - f(A) + \alpha - \text{EON} + \frac{c_T(T - T_{\text{ref}})}{RT} \quad (4)$$

where  $S$  is the salinity,  $K$  is a constant, ACN is the alkane carbon number or its equivalent (EACN) when the oil phase is not characterized by a pure hydrocarbon chain,  $f(A)$  is the contribution of the type and concentration of cosurfactant like alcohol,  $\sigma$  and  $\alpha$  are the characteristic parameters of the surfactants, EON is the number of ethylene oxide groups in nonionic cases, and  $(T - T_{\text{ref}})$  is the temperature difference relative to some reference temperature.<sup>39</sup> Each variable results in a change of at least one of the interaction energies of the surfactant with either aqueous or oil phase. For instance, an increase in salinity ( $S$ ) or surfactant lipophilic group length (and thus  $\sigma$ ) produces an increase in SAD, whereas an increase in the ACN of the oil phase or in temperature produces an opposite effect decreasing SAD in eq 3 for ionic surfactants.

The effect of the formulation variables on the emulsion properties has been studied using the SAD, considering similar amounts of water and oil and low quantities of surfactant.<sup>43</sup> Figure 11 summarizes the effect of the formulation variables on the type of emulsion, stability, interfacial tension, viscosity, electrolytic conductivity, and drop size, indicating the three phase region (Winsor type III phase behavior) with a shaded band in the middle of each diagram. On the abscissa of each portion of Figure 11 is the formulation scan shown in the upper left segment of the figure. When the formulation variable is increased from SAD < 0, a transition in the emulsion type from O/W to W/O and in the emulsion properties occur at SAD = 0, because the affinity of the surfactant switches from hydrophilic to lipophilic. The emulsion stability and viscosity undergo a minimum at SAD = 0, which is related to a low interfacial tension. The electrical conductivity decreases drastically inside the three phase region, indicating the phase inversion.

The previous representation of the effect of a single generalized formulation variable on the emulsion properties was extended by Salager et al.<sup>44</sup> to include the effect of the water–oil ratio at constant surfactant concentration in the form of a bidimensional map. Figure 12 shows a diagram of the bidimensional map, where the ordinate represents the generalized formulation variable SAD and the abscissa represents the water–oil ratio (WOR). From the diagram, it is possible to predict the emulsion type and the emulsion inversion based on the formulation variable and the WOR. The formulation divides the map in two halves, with the upper half corresponding to

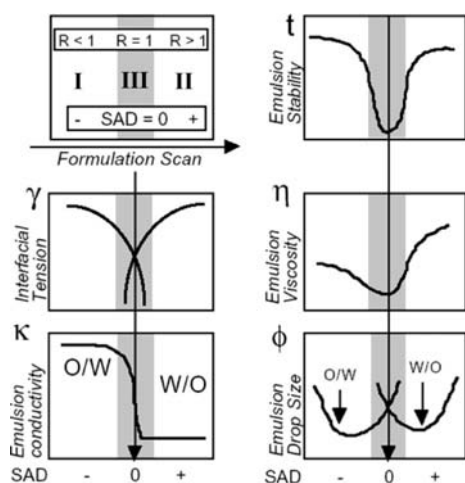


**Figure 12.** Diagram of generalized formulation-composition bidimensional map.<sup>40</sup>

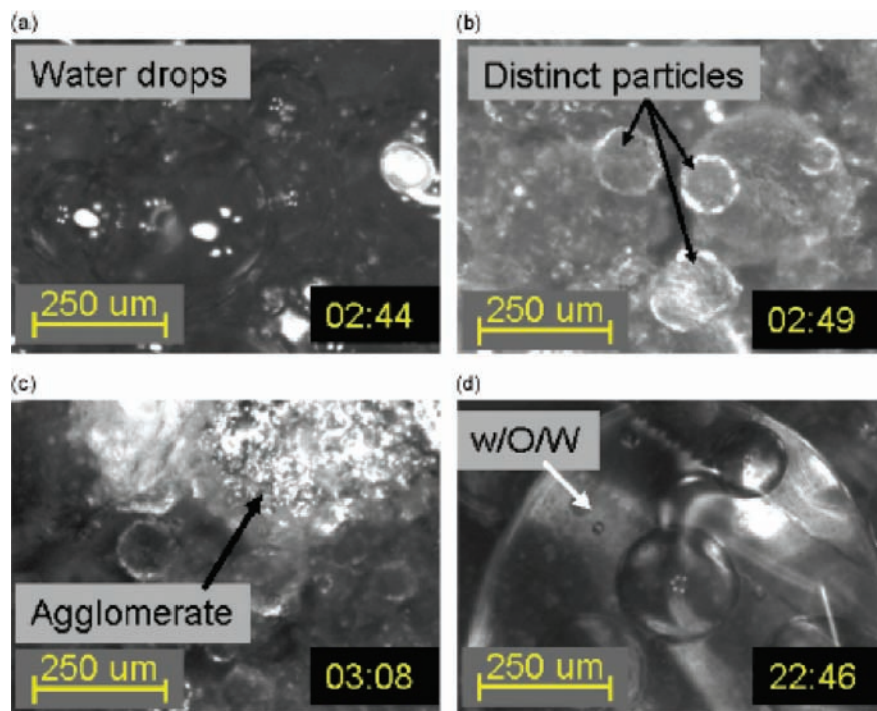
SAD > 0 suggesting a W/O emulsion, and a lower half corresponding to SAD < 0 suggesting an O/W emulsion. The WOR divides the map in three vertical sections: the left section represents low WOR (oil continuous emulsion), the right section represents high water content (water continuous emulsion), and the middle section will be controlled by the formulation. There are two sections where extreme WOR value causes formation of an emulsion type different from the one suggested by the formulation; these sections are associated with high instability and varying degrees of multiple emulsions. For the lower left zone (B-) with o/W/O (oil in water in oil) emulsions, the formulation suggests an O/W emulsion, but the excess oil becomes the continuous phase, hence resulting in a multiple emulsion that satisfies both trends. Similarly the upper right zone (C+) with w/O/W (water in oil in water) emulsions is where excess water is the continuous phase surrounding W/O emulsion droplets.

**Hydrates Formation in Emulsions.** In oil dominated flow-line systems, water-in-oil emulsions play a critical role in the formation and agglomeration of hydrate particles in pipelines. Previous studies have shown the formation of hydrates at the interface of water droplets, forming hydrate shells around the water droplet. In the study of gas hydrate formation with low water cuts (<35 vol%) in W/O emulsions using a laboratory-scale high-pressure autoclave cell and an industrial-scale flow loop, Turner<sup>3</sup> found that dispersed water droplets convert directly to hydrate particles (formed from the gas dissolved in the oil phase), maintaining the droplet size distribution during hydrate formation, and thus suggesting the formation of a hydrate shell at the water droplet interface; a particle size analyzer based on the focus beam reflectance method (FBRM)<sup>45</sup> was used to measure the water droplet and hydrate particle size distribution. To explain how the hydrates form in the water interface, Taylor et al.<sup>46</sup> studied hydrate film growth at a flat hydrocarbon/water interface using video microscopy combined with gas consumption measurements, using cyclopentane and methane as hydrate formers. From the hydrate film growth experiments, they proposed a hydrate film formation mechanism which consisted of three stages: (i) initial formation of a thin porous hydrate film propagating across the interface, (ii) film thickening over time growing into the water phase (shrinking core) and filling of the pores, and (iii) bulk conversion of hydrate film with filling of the remaining pores. It was also proposed that the hydrate film formation mechanism could be extrapolated to a water droplet interface following the same three stages and ending with full conversion of water (inside the shell) into hydrate over a long period of time.

Turner et al.<sup>47</sup> also developed a model to calculate hydrate growth in W/O emulsions that considered the hydrate shell formation around the water droplets followed by the conversion of the remaining water core to hydrate, in a mechanism similar to that described above. This model considered the mass transfer



**Figure 11.** Effect of formulation variables on type and properties of emulsions.<sup>39</sup>



**Figure 13.** PVM images of 68 vol% of water dispersed in crude oil: (a) initial W/O emulsion, (b) hydrate formation around water droplets, (c) large hydrate agglomerates during hydrate dissociation, (d) w/O/W emulsion after hydrate dissociation.<sup>45</sup>

limitations of methane across the boundary layer at the gas–oil interface, through the oil phase, and across the hydrate shell, to determine the hydrate growth rate in the interior of the water droplet, with the assumption of constant droplet size and ignoring heat transfer from the hydrate particles to the surroundings due to the exothermic heat of crystallization. The methane diffusivity through the hydrate shell was obtained from experimental measurements. The model gave a reasonably good fit to the experimental data, and even though the initial hydrate growth rate was underestimated and the long-term hydrate growth rate was overestimated, these errors were attributed to assumptions made in the development of the model.

**Effects of Hydrates in Emulsion Stability.** The formation and dissociation of hydrates can affect the stability of emulsions, leading to the generation of a free water phase from the agglomeration and coalescence of water dissociated from hydrate particles. The presence of a free water phase increases the risk of forming a hydrate plug in pipelines. Lachance et al.<sup>48</sup> studied the effect of hydrate formation and dissociation in the stability of W/O emulsions with different crude oils using differential scanning calorimetry (DSC). From the comparison of results obtained with four crude oils, they found that hydrate formation and subsequent dissociation destabilized W/O emulsions in oils with a low fraction of asphaltenes or when a high concentration of resins prevented the deposition of asphaltenes onto the water droplet interface, while oils with a higher fraction of asphaltenes resisted destabilization. They proposed a hydrate-induced destabilization mechanism which consisted of a formation step, where hydrate encrusted water droplets agglomerate, and a dissociation step, where the release of the gas molecule causes the interface to break resulting in coalescence of adjacent droplets. The resistance to destabilization by oil with higher fractions of asphaltenes can be explained by the formation of a rigid cross-linked network adsorbed at the droplet interface.

In high water (>35 vol%) content W/O emulsions, the formation and dissociation of hydrates also affect the emulsion stability, leading to an inversion of the emulsion from W/O to

O/W or the generation of multiple emulsions. Greaves et al.<sup>49</sup> studied emulsions with water content greater than 60 vol% in a high-pressure autoclave cell equipped with two particle size analyzer probes (focus beam reflectance method [FBRM] and particle video microscope [PVM]). With reference to Figure 12, these emulsions can be located in the upper half of the bidimensional map ( $SAD > 0$ ) and near the vertical inversion line. In a mechanism similar to that proposed by Lachance et al.,<sup>48</sup> hydrate encrusted water droplets first agglomerated and then coalesced during dissociation, causing the appearance of an aqueous continuous phase due to the large amount of water in the system, destabilizing the W/O emulsion to form a w/O/W emulsion. Greaves et al.<sup>49</sup> also showed using in situ high pressure particle imaging analysis (from the PVM) that hydrate dissociation can result in extensive hydrate agglomeration (see Figure 13 of PVM images of hydrate agglomeration during hydrate dissociation), thereby confirming the calorimetric results by Lachance et al.<sup>48</sup> which indicated that hydrate dissociation can lead to emulsion destabilization and hydrate particle agglomeration.

**Agglomeration Mechanisms of Hydrate Particles.** Different mechanisms have been suggested for the agglomeration of hydrate particles in oil dominated systems. From the expected hydrophilic character of the hydrate surface, it was suggested that capillary forces, formed by a liquid bridge, hold the particles together.<sup>50</sup> The capillary bridge theory<sup>51</sup> was used as an explanation of hydrate particle agglomeration in investigations of micromechanical force measurements between two hydrate particles, which increased when the temperature was raised toward the melting temperature, and a quasi-liquid water layer formed at the particle surfaces.<sup>52,53</sup> The capillary bridge was also observed in the study of micromechanical adhesion forces between hydrate particles and pipeline solid surfaces with a water drop deposited on the solid surface,<sup>23</sup> increasing the adhesion force to more than 10 times that between hydrate particles, indicating possible deposition of hydrates on pipe walls through this mechanism.

According to the capillary bridge theory, the capillary force between two hydrate particles is proportional to the interfacial tension between the bridging liquid water and the continuous oil phase. A decrease in the interfacial tension between water and oil decreases the capillary forces and prevent the agglomeration of hydrate particles that may be separated by shear forces during flow; this is one of the principles of antiagglomeration agents (or antiagglomerants).

From studies of hydrate slurry viscosity,<sup>54</sup> a hydrate agglomeration mechanism was proposed which includes crystallization of a water droplet by the contact with a hydrate particle, and growth of the resulting agglomerate with the subsequent contact of water droplets. This mechanism was used for the development of a hydrate slurry rheology model by Camargo and Palermo,<sup>55</sup> in which the viscosity of the hydrate slurry increases with agglomerate size. The adsorption of a surfactant on the hydrate particle surface can prevent the contact with water droplets and other hydrate particles by changing the wettability of the hydrate particle surface to oil-wet and by creating steric repulsions; this is another principle of antiagglomerants.

The complete elimination of interfacial agglomeration mechanisms of hydrate particles, like liquid bridging, has been the principle of new technologies referred to as the stabilized cold flow concept, in which flowable slurries of dry hydrate particles are generated.<sup>56–59</sup> The conversion of excess free water into small and dry hydrate particles is the key to eliminate all chances of agglomeration in the stabilized cold flow concept.

**Formulation Dependence of Hydrate Antiagglomeration Agents.** Antiagglomerants are surfactants which have the purpose to disperse hydrate particles in the oil phase and keep them apart, preventing agglomeration. Some mechanisms that contribute to the antiagglomeration of solid hydrate particles are common to stabilization of emulsions, such as steric repulsions. Other mechanisms involved in the antiagglomeration of hydrates consider the nature of the agglomeration phenomenon, which can be different from the emulsion rupture mechanism; studies on antiagglomerants indicate that emulsification is not required for an effective antiagglomerant.<sup>60,61</sup> From a theoretical analysis of the forces in agglomeration and stabilization of hydrate particles (i.e., capillary and dispersion forces), Anklam et al.<sup>62</sup> concluded that an effective antiagglomerant is one that: (a) reduces the size of hydrate particles through the reduction of water droplet size in the W/O emulsion, (b) decreases the interfacial tension between water and oil phases to reduce capillary bridge forces, and (c) modifies the water wettability of the hydrate surface to oil-wet by increasing contact angle through the water phase. These features for an effective antiagglomerant agent can be attained considering the effect of formulation variables on emulsion properties, tailoring the surfactant mixture to a particular system, using as a reference a diagram like the one presented in Figure 11, where the formulation conditions that provide minimum droplet size, low interfacial tension, and low emulsion viscosity can be identified.

Effects of formulation variables on antiagglomerant surfactants have been published in a limited number of papers. York and Firoozabadi<sup>60</sup> studied the effect of adding salt (NaCl and MgCl<sub>2</sub>) on the antiagglomeration efficiency of an anionic quaternary ammonium salt and a nonionic rhamnolipid surfactant, in a model oil/water/tetrahydrofuran system (where tetrahydrofuran is a model hydrate former). They observed that the addition of salt (NaCl or MgCl<sub>2</sub>) eventually results in agglomeration of hydrates, with bivalent salts (MgCl<sub>2</sub>) being more detrimental, and nonionic biosurfactants being more effective at lower salt concentrations than the anionic surfactant.

The addition of both salts tested increased the SAD, making the surfactant more lipophilic with less adsorption at the interface. With the anionic surfactant, agglomeration was observed at low salt (NaCl and MgCl<sub>2</sub>) concentrations and high surfactant concentrations, restoring antiagglomeration behavior with the addition of salt until a point where agglomeration was observed again, indicating a range of concentrations with good antiagglomeration behavior. Others also studied the effect of salt on antiagglomerants,<sup>63</sup> but reported an improvement in antiagglomeration performance when increasing salt concentration, which is attributed to thermodynamic inhibition of hydrates by the increased concentration of salt in the unconverted water phase.<sup>61</sup>

The addition of low concentrations of an alcohol, which acts as a cosurfactant, can change the formulation improving the antiagglomeration property of some surfactants. The addition of MeOH (0.5–5.0 wt %) as a cosurfactant has been proven, at laboratory scale, to decrease the required concentration of antiagglomerant surfactant, maintaining the antiagglomeration properties of the system.<sup>61,63</sup> In one study,<sup>61</sup> the improved antiagglomeration characteristic was explained by a synergistic contribution of MeOH that increased the surfactant density at the interface, reducing further the interfacial tension, and thereby decreasing water droplet size conducting to small hydrate particles. This change in the formulation modified the emulsion properties to coincide with a minimum in droplet size as shown in Figure 11. In another study,<sup>63</sup> it was shown that antiagglomeration was improved by adding 15 wt % of MeOH and 0.5 wt % of (unidentified) antiagglomerant to a system with 80% water cut, explaining the antiagglomeration improvement by the increase of MeOH concentration in the free water phase that thermodynamically inhibits further formation of hydrates.

## Summary

Typical hydrate prevention methods, based on shifting the hydrate equilibrium phase boundary by adding thermodynamic inhibitors, focus on the treatment of the aqueous bulk phase requiring large concentrations of methanol or monoethylene glycol. The gas and oil industry is currently in a transition from hydrate avoidance to risk management with the use of inhibitors that act at the interfaces of hydrate particles (kinetic hydrate inhibitors and antiagglomerants), which has been proven to reduce the required concentrations of chemical additives, i.e., a more economical approach. This fact highlights the importance of considering surfaces and interfaces in the study of gas hydrates.

Revisiting the conceptual model for hydrate formation in a multiphase flow system consisting of water, oil, and gas presented in Figure 1, it is found that interfaces between water and hydrocarbon phases are ideal locations for gas hydrate formation, and that interaction mechanisms between hydrate particles and solid surfaces may or may not result in the blockage of pipelines, depending on several factors, such as oil composition (presence of natural surfactants), wettability of solid surfaces, formulation variables and their effect on antiagglomerants performance, presence of free water, and particle size among others. Understanding the fundamental concepts of surface chemistry, in particular surfactants (molecules with preference to interfaces) and emulsions (mixtures of two immiscible fluids with abundant surface area), is of great value for the research, design, and development of novel techniques for the management of gas hydrates in oil and gas pipelines.

In this review the relationship between surface chemistry and gas hydrates was presented using a number of studies available

in the technical literature to provide a clear connection of the current advances in the study of hydrates with interfacial phenomena.

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### Appendix

#### Nomenclature

$A_{CO}$  = Net interaction energy of the surfactant with the oil phase  
 $A_{CW}$  = Net interaction energy of the surfactant to the aqueous phase  
 CMC = Critical micelle concentration  
 DSC = Differential scanning calorimetry  
 FBRM = Focus beam reflectance method  
 HLB = Hydrophilic–lipophilic balance  
 O/W = Oil-in-water emulsion  
 o/W/O = Oil-in-water-in-oil multiple emulsion  
 PVM = Particle video microscope  
 R = Winsor ratio of net interaction energies of surfactant to aqueous and oil phases  
 SAD = Surfactant affinity difference or balance  
 SARA = Saturates, aromatics, resins, asphaltenes  
 SDS = Sodium dodecyl sulfate  
 W/O = Water-in-oil emulsion  
 w/O/W = Water-in-oil-in-water multiple emulsion  
 WOR = Water–oil ratio  
 $\mu_w^o$  = Standard chemical potential of the surfactant in the water phase  
 $\mu_o^o$  = Standard chemical potential of the surfactant in the oil phase

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