

Partitioning of Multi-Component Surfactants Systems in Oil and Water

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ABSTRACT

Many production chemicals are complex mixtures of surfactants yet are described by a single partition characteristic such oil soluble or water soluble. This paper presents a simple model of multi-component surfactant mixture partitioning based on the work of Zhu and Free. The model is extended to show how the composition of the production chemical changes as the oil/water ratio changes. The results show that the composition of the original production chemical in either the oil or water phases is rarely the same as the neat product on injection and can vary substantially as the water-cut changes over the production life and through the production system.

Key words: Multi-component, Surfactant, Partitioning

INTRODUCTION

Production chemicals used in the oil and gas industry are often multi-component surfactants which will partition between the oil and water often with different partition coefficients. As a consequence of the different partition coefficients, the proportion of each component in either the oil phase or the water phase will change as the water cut changes. A simple model has been developed to illustrate the compositional changes in the oil and water phase over the water-cut range.

The model is an extension of the work of Zhu and Free, and clearly shows how the ratio of the components in either the oil or water phases rarely matches the composition ratio in the neat product.¹ As a result, if the performance of a production chemical is tested in a single phase e.g. corrosion inhibitor testing in brine only, the composition ratio of the components is unlikely to reflect what will be found under field application.

MODEL DEVELOPMENT

Partition Coefficient

Some of the equilibria associated with the physical chemistry of surfactant corrosion inhibitors are discussed in Woollam et al., and Zhu et al. and summarized in Figure 1.^{2,3} In the discussion and in the model development it is assumed only the partition coefficient, $P_{o/w}$, characterizes the ratio of the concentration of a given component in the oil versus that in water, that is there are no other interaction parameters which would impact this ratio.

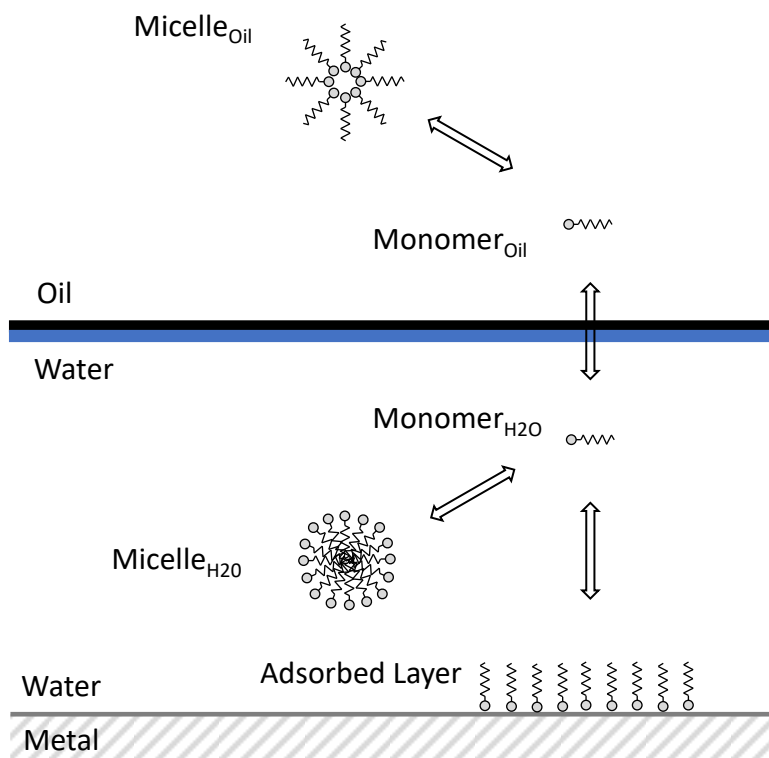


Figure 1: The Equilibria Associated with the Partitioning, Adsorption and Dissociation of a Surfactant in an Oil and Water System

Note, a significant assumption of this model is that concentrations of the components in either the oil or water phases are below that critical micelle concentration (CMC) in each phase. As a consequence, the distribution of surfactant is described solely by the linear partition coefficient as opposed to the non-linear distribution coefficient which includes all forms of a molecule when calculating the concentration in a given phase – see Woollam.²

Surfactant Addition

For a given component of the surfactant, when a known amount is added based on the total volume of the then by mass balance is given by,

$$C_T V_T = C_w V_w + C_o V_o \quad [1]$$

Note that the left-hand-side (LHS) is the non-equilibrium amount added whereas the right-hand-side (RHS) is the equilibrium concentrations in the oil and water phases which is

unknown but is related to the partition coefficient. For a multi-component surfactant addition, then an individual component, i , is described in terms of the mole fraction in the total, x_i , of the total amount added,

$$x_{T,i}C_TV_T = C_{W,i}V_W + C_{O,i}V_O \quad [2]$$

Where $C_{W,i}$ and $C_{O,i}$ are the concentrations of the monomer for component i in the water and oil phases, respectively.

Component Partition Coefficient

The partition coefficient is defined as the ratio of the concentration of a species in one phase versus another giving the following expression,⁴

$$P_{O/W,i} = \frac{C_{O,i}}{C_{W,i}} \quad [3]$$

Substitution in Equation [2] yields,

$$x_{T,i}C_TV_T = C_{O,i} \left(\frac{V_W}{P_{O/W,i}} + V_O \right) \quad [4]$$

Or,

$$C_{O,i} = \frac{P_{O/W,i}x_{T,i}C_TV_T}{(V_W + P_{O/W,i}V_O)} \quad [5]$$

Similarly, the concentration in the water phase can be calculated as,

$$C_{W,i} = \frac{x_{T,i}C_TV_T}{(V_W + P_{O/W,i}V_O)} \quad [6]$$

Using Volume Fraction

Using the volume fraction rather than absolute volume we have,

$$\frac{V_O}{V_T} + \frac{V_W}{V_T} = 1 = \phi_O + \phi_W \quad [7]$$

And the concentration terms, substituting $\phi_O = 1 - \phi_W$, for oil and water respectively become,

$$C_{O,i} = \frac{P_{O/W,i}x_{T,i}C_T}{(\phi_W + P_{O/W,i}(1 - \phi_W))} \quad [8]$$

$$C_{W,i} = \frac{x_{T,i}C_T}{(\phi_W + P_{O/W,i}(1 - \phi_W))} \quad [9]$$

Mixture Apparent Partition Coefficient

Zhu and Free defined the partition of a mixture or apparent partition coefficient as sum of the individual components in each phase given by,¹

$$P_{O/W,Mix} = \frac{C_{O,Total}}{C_{W,Total}} = \frac{\sum C_{O,i}}{\sum C_{W,i}} = \frac{\sum \frac{P_{O/W,i} x_{T,i} C_T}{(\phi_W + P_{O/W,i} (1 - \phi_W))}}{\sum \frac{x_{T,i} C_T}{(\phi_W + P_{O/W,i} (1 - \phi_W))}} \quad [10]$$

Model Parameters

The surfactant mixtures composition and component partition coefficients used in the numerical experiments are shown in Table 1 and Table 2.

For each corrosion inhibitor composition, the water volume fraction was varied from 0 - 1 and the total concentration added, $C_T = 1$ in order to give normalized results.

Table 1
Idealized Corrosion Inhibitor (1) Composition and Component Partition Coefficient

		Component				
Index	i	1	2	3	4	5
Mole fraction	x_i	0.20	0.20	0.20	0.20	0.20
Partition coefficient	$P_{O/W,i}$	0.10	0.33	1	3.33	10

Table 2
Model Corrosion Inhibitor (2) Composition and Component Partition Coefficient

		Component				
Index	i	1	2	3	4	5
Mole fraction	x_i	0.20	0.45	0.15	0.15	0.05
Partition coefficient	$P_{O/W,i}$	0.05	0.20	10	50	200