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Phase volume effects in the sub- and super-CMC partitioning of nonionic surfactant mixtures between water and immiscible organic liquids

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ABSTRACT

It is a widely held misconception that surfactant phenomena involving adsorption or partitioning between phases plateau at aqueous concentrations beyond the surfactant critical micelle concentration (CMC). While this is generally true for single-component surfactants, it has been recognized for some time that mixed surfactants can deviate from this behavior, in some cases to dramatic extents. This paper examines the influence of phase volume ratios on both the sub- and super-CMC partitioning of a nonionic surfactant mixture between water and tetrachloroethylene (PCE). Partitioning was measured in batch systems with phase volumes ratios of water (w) to PCE (organic liquid, o) ranging from V_w:V_o = 10:1 to 1:2. Results show a strong dependence of total surfactant partition coefficient ($K_{apparent}$) on phase volume, with more than a factor of four increase in $K_{apparent}$ from the 1:2 system to the 10:1 system. All systems also show considerable increase in partitioning beyond the CMC of the mixture remaining in water (CMC_{mix}), with continued partitioning increases observed to concentrations more than two orders of magnitude beyond CMC_{mix}. Results also show continued change in surfactant composition in both phases with increasing concentration beyond CMC_{mix}.

Measured partitioning results were used to determine partition coefficients and pure component CMC values for all surfactant components in the mixture, and then these values were used to model mixed surfactant partitioning controlled by mixed micelle formation. Model results show that the mathematics of mixed surfactant partitioning quantitatively describes both the effect of phase volume on partitioning, and the continued increase in partitioning beyond CMC_{mix}. From the model it is apparent that regardless of phase volume (and its effect on $K_{apparent}$), the high-concentration asymptotic partitioning plateau is independent of phase volume, although broadly distributed surfactant mixtures may not reach the plateau at physically possible concentrations. Equations are presented for calculating high and low-concentration asymptotic values for partitioning and EO averages.

A novel method for simultaneous, direct measurement of $\gamma^i CMC^i$ (the product of the micellar activity coefficient and pure component CMC) for all surfactant components in a mixture is presented.

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1. Introduction

When an aqueous surfactant solution comes into contact with an immiscible organic liquid, surfactant monomers partition into the organic liquid until equilibrium is reached between the two liquids. For hydrophilic surfactants, the formation of micelles in aqueous solution limits the concentration of surfactant monomers in solution, limiting the driving force for partitioning into the organic liquid. In single-component surfactants, this causes partitioning to plateau at aqueous concentrations beyond the critical micelle concentration (CMC), as a result of constant monomer concentration with increasing total surfactant concentration. However, it has been known for some time that when mixed surfactants partition between water and an organic liquid, the total amount of surfactant partitioned into the organic liquid continues to increase beyond the mixed surfactant CMC, and the surfactant phase compositions continue to change with increasing concentration (e.g., [1–5]). In a 2000 paper, Cowell et al. [3] studied the high-concentration bulk partitioning of a range of commercial nonionic surfactant mixtures. They found that partitioning continued to increase to aqueous concentrations more than 100 times the CMC for some surfactant/solvent combinations. The amount of the partitioning increase they observed was substantial, with partitioning increasing in some cases to an order of magnitude or more beyond the amount of partitioning observed at the CMC. At that time it

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was speculated that the effect was the result of surfactant polydispersity and mixed micelle formation, but the work provided only qualitative evidence.

Another interesting phenomenon that has been previously reported is that the partitioning of mixtures can depend on the phase volume ratio, with vastly different surfactant compositions in the phases resulting at different phase volume ratios [5,6]. To date, this phenomenon has received little reported quantitative study. Furthermore, work examining the effect of this phenomenon on the resulting total extent of high-concentration partitioning has not been reported.

The objective of this work was to examine mixed surfactant partitioning, with emphasis on the effects of phase volume ratio on low-concentration (sub-CMC) and high-concentration (super-CMC) partitioning behavior. The hypothesis driving the work was that both sub- and super-CMC partitioning can be quantitatively predicted by modeling mixed surfactant partitioning and mixed micelle formation.

2. Materials and methods

2.1. Materials

The chlorinated alkene tetrachloroethylene (PCE), was used in this study due to its widespread use and relevance, and because preliminary measurements indicated that partitioning of nonionic surfactants was likely to be high enough to allow the precise measurements needed for this work. Previous reported work examining mixed partitioning has used more hydrophobic solvents (e.g., *iso*-octane, *n*-hexane, *n*-heptane [1–12]), so the use of PCE also provides new quantitative information not previously available. Tergitol NP15, a commercial nonylphenol ethoxylate with a reported average of 15 EO units per molecule was provided by Dow Chemical Co. (Midland, MI), and was used as received. Characterization of NP15 was conducted using the HPLC method described in the next section. Based on HPLC analysis, NP15 was found to have an average of 14.66 ± 0.018 EO units per molecule (95% confidence interval), based on seven separate injections (full distribution details are provided in the accompanying Supplementary material). NP15 was selected because its mixed behavior has been found to be quantitatively comparable to other ethoxylated nonionic surfactants (e.g., [13–15]), and its chemical structure allows for fluorescence detection, making it suitable to the highly sensitive measurements conducted here.

2.2. Instrumental analyses

Bulk surfactant concentrations were analyzed using a Shimadzu model UV-1601 spectrophotometer (Shimadzu Corp., Tokyo, Japan). A full-spectrum analysis technique [16] was used to ensure that absorbance of dissolved PCE did not interfere with surfactant concentration measurements. The method uses a nonlinear optimization routine to find the linear combination of standard spectra of absorbing species (in this case, NP15 and PCE) that provides the best fit to the measured sample spectrum. The application of Beer's law across the full spectrum provides highly reproducible measurements of concentrations of absorbing species. The method has been previously used for analysis of pharmaceutical compounds [16,17], and nonionic [18] and anionic [19] surfactants, among other applications. For all analyses, sample supernatants were diluted to appropriate concentrations so that the important nonylphenol spectral peaks did not saturate the detector, and could be included in analyses. From the standpoint of partitioning experiments (discussed below), no dilution was necessary for the 5–6 lowest concentration samples, with the number of samples depending on phase volume ratio; samples not needing dilution for analysis included all of the sub-CMC samples. Dilutions as high as 80:1 were needed for the highest concentration samples (initial aqueous surfactant concentrations covered a three order-of-magnitude concentration range).

Although the full spectrum analysis method is capable of simultaneously detecting multiple compounds in mixtures, it cannot be applied to the individual ethoxylated components of nonylphenol ethoxylates because all of the components have the same chromophore. As such, an adsorption HPLC method was used. The method was modified from a previously reported method [20] which has been used for study of the adsorption of ethoxylated alcohols and alkylphenol ethoxylates to solid surfaces [13–15,21]. For this work, a 3.2 mm × 250 mm Jones Chromatography Apex (Grace Davison, Deerfield, IL) silica column with 5 μm particle size was used. A hydrophobic 3.0 mm × 7.5 mm Alltech Alltima C18 precolumn (Grace Davison) was used to prevent premature breakthrough of low-EO components when aqueous surfactant samples are injected (essentially an inline extraction; see Ref. [20]). The C18 precolumn, in combination with the use of traditionally reversed phase solvents, allows the direct injection of aqueous samples without the need for intermediate preparation steps. Prior to use, the silica column was prepared by flushing with isopropanol, since the normal-phase eluents typically shipped in silica columns are immiscible with water and acetonitrile. Measurements were conducted using a Shimadzu (Columbia, MD) Class VP HPLC gradient system. Both flow rate and solvent composition were varied during runs. The solvent composition was held at 100% acetonitrile until 1 min following injection, and then ramped linearly to a composition of 65% acetonitrile, 35% water at 43 min. At 43 min, the solvent composition was returned to 100% acetonitrile and held there until 50 min to prepare the column for the next run. The flow rate was held at 0.3 mL/min for the first minute, and then ramped to 0.6 mL/min at 37 min, where it was held until 43 min, when it was changed to 0.3 mL/min for the remainder of the run. For this work, fluorescence detection was used, with a Shimadzu RF-10Axl variable wavelength fluorescence detector set to an excitation wavelength of 202 nm, and an emission wavelength of 311 nm. Fluorescence detection was selected due to its excellent linearity and its insensitivity to PCE. Injection volume of each sample was adjusted so maximum peak height was approximately 80% of maximum fluorescence for all but the one-to-two lowest concentration samples at each volume ratio, which were limited by maximum possible injection volume. This approach reduced the possibility of any systematic error due to surfactant mass injected. Calculation of individual surfactant component concentrations was achieved by multiplying bulk concentrations determined from full-spectrum UV absorbance measurements with component distributions determined from HPLC analysis.

Integrations of chromatograms were conducted using a modified Gaussian fitting routine to deconvolute slightly overlapping peaks. The method is described in the accompanying Supplementary material. Ultimately, results with the routine were quantitatively indistinguishable from results calculated based on integrations done by the Shimadzu Class VP Ver. 4.1 software, but showed slightly better injection-to-injection variability, particularly for low area peaks, at the edges of the surfactant distribution.

Because the HPLC method used is a gradient method, the fluorescence response of NP components varies slightly during elution as the solvent composition passing through the detector, as the location of the peak corresponding to maximum excitation shifts. This effect was quantified by direct injection of NP15 in different solvent composition eluents in the absence of a column, and included in calculations. Ultimately, this correction has very little effect on

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