

# Determining Octanol/Water Partitioning Coefficients for Industrial Surfactants

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## ABSTRACT

Log $P_{ow}$  studies were conducted on a number of alcohol ethoxylate surfactants (AES) with hydrophobic chain lengths varying from five to 14, and the numbers of ethoxylate groups ranging from three to eight. From these studies, the relationships between the hydrophobic chain length and the number of ethoxylate groups with the surfactant's log $P_{ow}$  were established. This allowed the prediction of log $P_{ow}$  values for other AES, not included in this study. The majority of surfactants used in the industry have wide distributions of hydrophobic and/or hydrophilic functionalities. Experimentally determining the partitioning coefficient for each individual molecule can be difficult and time-consuming. Yet in many cases, obtaining the surfactant's log $P_{ow}$  is a crucial step in gaining approval from regulatory agencies for use in particular environments. This method allows the use of experimental data from monodisperse related molecules to calculate log $P_{ow}$  values for complex surfactant mixtures.

# INTRODUCTION

When considering the use of offshore well-construction chemicals, one of the key tools used by environmental regulators is the application of ecotoxicity testing. In addition to internal pressures to regulate, some countries have signed international conventions requiring legislation in compliance with their obligations. Examples of this are the Oslo and Paris Commission (OSPAR) impacting the North East Atlantic (North Sea), the Barcelona Convention, which covers the Mediterranean Sea, and the Helsinki Commission (HELCOM), which covers the Baltic Sea.

Mandated ecotoxicity testing includes physical properties such as biodegradation, toxicity, and bioaccumulation, which are used to evaluate the chemical's environmental impact. These properties are the mainstays of many regulatory programs, and the tests used differ significantly between regions and industries.

Well-established test methods are available for measuring these properties. In particular, toxicity and biodegradation test methods are applicable to all chemicals. The accepted methods for experimentally measuring the bioaccumulation of chemicals are expensive and require testing on living organisms (1, 2). Rather than nurture and then later destroy the organisms used for testing, the preferred technique is to predict bioaccumulation potential from experimentally determined octanol/water partition coefficients ( $\log P_{ow}$ ) (3–5). The Organization for Economic Co-operation and Development (OECD) has outlined three accepted guidelines for predicting bioaccumulation: OECD 107, OECD 117, and OECD 123. These guidelines are applicable to all classes of chemicals except for surface active chemicals (surfactants). These test method limitations have been imposed mainly because of the inherent ability of surfactants to self-associate, stabilize emulsions, foam, and concentrate at an oil/water interface. In addition, many commercial surfactants are mixtures of materials, though many pure surfactants can be obtained in small quantities.

In OECD 117, a high performance liquid chromatography (HPLC) method, the retention time of the chemical of interest is compared to retention times of reference samples with similar structures and known  $\log P_{ow}$  values (3). For nonsurfactants, retention times are normally determined by the molecule's relative affinities for the mobile and stationary phases and are directly related to a molecule's  $\log P_{ow}$ . However, the retention times for surfactants are also dependent upon the surfactant's preference for surfaces and interfaces, which invalidates this method. OECD 107, the shake flask method, is not appropriate to determine the partition coefficients of surfactants because the presence of surfactants can lead to micro-emulsions and octanol droplets in the water layer (4). This results in an overestimation of the quantity of surfactant present in the water layer and the computation of erroneous partition coefficients (6). OECD 123, a slow-stir method, was developed to address some of the limitations of OECD 107; namely the formation of octanol droplets in the water phase and the associated foaming of the two layers incurred when shaking the test flask, yet this guideline still does not apply to surfactants (5).

In addition to the above mentioned concerns with current  $\log P_{ow}$  methodology, it is still argued that true partition coefficients do not exist for surfactants. A common opinion is that a

significant portion of surfactant molecules in a given test mixture is present at the octanol/water interface and adsorbed to the glassware surfaces. This is often perceived as invalidating any  $\log P_{ow}$  results even though they would be valid if the concentrations of surfactant in both the oil and water were measured. Recently, methods have been developed that address all of these concerns with surfactant  $\log P_{ow}$  measurements (7, 8). Test vials and other experimental conditions are chosen so that negligible quantities of surfactant are adsorbed at the octanol/water interface. Percent recoveries are also determined to prove that the majority of the surfactant is in solution rather than adsorbed in the glassware.

For accurate measurements of a partition coefficient for a surfactant, the concentration of the test substance must be lower than the critical micelle concentration (CMC). This alleviates all concerns with the presence of micelles during  $\log P_{ow}$  testing. However, measuring the CMC of a surfactant when both oil and water are present requires care. Two techniques are especially useful. The first is dynamic laser light scattering (DLS). This technique measures the diffusion coefficient (and hence size) of scattering particles such as micelles or oil drops. When micelles are present, the concentration of surfactant in solution would be considered above the CMC (9–18). Serial dilutions can be made until the micelles can no longer be detected. This technique works well in highly purified water. When measuring the CMC in water that has been previously saturated with n-octanol, the octanol can change the shape and swell any micelles present, and this is reflected in the DLS data. An alternative approach is to use the inverted, vertical-pull surface tension method for measuring CMC values (19–22). This technique works well with both pure water and water saturated with n-octanol.

## **EXPERIMENTAL**

### **Chemicals and Test Compounds**

The surfactants and n-octanol used in this study were purchased from Aldrich (St. Louis, MO). All water used was purified through a Milli-Q Gradient A10 from Millipore (Billerica, MA). The pH of the water after purification was 6.4. For the slow-stir experiments, both the octanol and water solutions had been presaturated with the other liquid for 24 hours.

### **Liquid-Chromatography Mass-Spectrometry (LC-MS) Analysis**

A 1100 series HPLC and G1946D MSD from Agilent (Palo Alto, CA) were used to measure the amounts of surfactant present in each layer. The column used to separate the surfactant from octanol and other portions of the solvent was a  $100 \times 4.6$  mm Luna  $3\mu$  C18(2) column from Phenomenex (Torrance, CA). The eluent was an acetonitrile/0.1 M ammonium formate (95/5) solution. The column temperature was held at 30°C and separation conditions are outlined in Table 1.

### **Slow-Stir Test Method**

The slow-stir method for measuring  $\log P_{ow}$  values used in this study was adopted and modified from the original publication by Brooke and Williams (23). These modifications are outlined in the work by Karcher et al. (7, 8).

# RESULTS AND DISCUSSION

## Number of Surfactant Molecules at an Octanol/Water Interface

One of the concerns in regards to determining partition coefficients of surfactants is their surface active properties. To demonstrate that the number of surfactant molecules at the octanol/water interface is a very small fraction of the total number of surfactant molecules in each slow-stir sample, the actual percentage of molecules at the interface was calculated. The slow-stir vessels used in this study have an inner diameter of 4.4 cm. Therefore, the surface area of the octanol/water interface was calculated to be  $15.2 \text{ cm}^2$  ( $1.52 \times 10^{17} \text{ \AA}^2$ ). The area per molecule for a number of alcohol ethoxylates were previously measured with neutron reflection and were reported to range from  $33\text{--}72 \text{ \AA}^2$  for molecules with 2–12 ethoxylate groups (24). By dividing the area per molecule into the surface area of the vessel, the maximum number of molecules that may be present at the octanol/water interface at any given time can be calculated.

The number of molecules in the vessel was calculated by multiplying the molar concentration of surfactant with the volume of water used and Avogadro's number. Finally, the percentage of molecules at the interface was determined by dividing the number of molecules at the interface by the total number of molecules in solution and multiplying by 100%.

## Slow-Stir $\text{LogP}_{ow}$ Test Method

For each surfactant, two separate slow-stir samples were prepared at two different concentrations. A single stock solution was prepared for each surfactant using octanol saturated water or water-saturated octanol. Before the addition of surfactant, the appropriate volumes of water and octanol were added to slow-stir vessels and allowed to slow-stir for 24 hours. After 24 hours, the desired volume of stock solution to be added to the test vessels was determined and an equal volume was removed from the appropriate layer in the slow-stir vessel. An identical volume of the stock solution was then added to each vessel. The more dilute sample had half the amount of sample as the more concentrated sample. Standards were prepared with concentrations ranging from 1–50  $\mu\text{g/l}$ .

The samples were slow-stirred at 130 rpm and held at  $23^\circ\text{C}$  for the duration of each experiment. A sample was taken from both the water and octanol layers of each sample every 24 hours until the samples reached equilibrium and remained at equilibrium for a 72-hour period. The sample was taken from the water layer first, and then a sufficient aliquot was removed from the octanol layer with a micropipette so that the water/octanol ratio remained unchanged. Light-scattering data was generated from the water layer to detect the presence of micelles or n-octanol droplets in the water layer. Any data obtained in the presence of micelles or n-octanol droplets was disregarded.

The samples were then diluted with a 95/5 solution of acetonitrile and 0.1 M ammonium formate for analysis on the LC-MS. The samples were diluted so that the final concentrations were between 1 and 50  $\mu\text{g/l}$ . For each surfactant, approximately 250  $\mu\text{l}$  of the aqueous samples were diluted to 1,000  $\mu\text{l}$ . Often it was necessary to dilute the octanol samples twice. In most

cases, between 10 and 20  $\mu\text{l}$  of the sample were diluted to 1,000  $\mu\text{l}$ , which was followed by a second identical dilution.

## Surfactant Analysis

The amount of surfactant present in each sample was determined using a HPLC equipped with a MS. A mixture (95/5) of acetonitrile and 0.1 M ammonium formate was used as the eluent. A C18-based column was used to facilitate separation between the surfactant and solvent and an isocratic flow between 0.5 and 0.8 ml/min was used. The MS was used in single-ion mode and the ammonium adducts  $[\text{M-NH}_4]^+$  were detected. Detection limits with these parameters for most of the surfactants were well below 1  $\mu\text{g/l}$ . Calibration curves were constructed for each surfactant to facilitate the quantification of surfactant in each slow-stir sample.

## Slow-Stir Data Analysis and Interpretation

Each prepared sample was injected twice on the LC-MS. The average peak area was used to calculate the amount of surfactant in each sample. The concentrations of surfactant in both the water and octanol layers were then calculated for each slow-stir sample after appropriate adjustments were made according to each dilution factor. Once the slow-stir concentrations were determined,  $\log P_{\text{ow}}$  values were calculated for each surfactant.

In addition to calculating the  $\log P_{\text{ow}}$  for each surfactant, the percentage of recovered surfactant was determined. The mass of surfactant present in solution was calculated for each sample by multiplying the concentration in the water layer by the volume of water, multiplying the concentration in the octanol layer by the volume of octanol, and adding the two together. The percentage of recovered surfactant was then determined by dividing the mass of surfactant present in solution by the mass of surfactant added to the slow-stir vessels.

## Predicting $\log P_{\text{ow}}$ for Other AES

The experimental  $\log P_{\text{ow}}$  values were plotted against both carbon chain length and the number of ethoxylate groups. The resulting plots showed a direct relationship between both carbon chain length and the number of ethoxylate groups with  $\log P_{\text{ow}}$ . Increasing the carbon chain length results in higher  $\log P_{\text{ow}}$  values, while increasing the number of ethoxylate units results in lower  $\log P_{\text{ow}}$  values. Ideally, one would prefer to analyze a number of pure surfactants with identical carbon chain lengths and differing ethoxylate units, as well as a number of surfactants with identical numbers of ethoxylate units and differing carbon chain lengths to better understand the relationship between these structural properties and  $\log P_{\text{ow}}$ .

However, because of the limited availability of pure AES, only a few surfactants in each series were obtained. Three surfactants with different numbers of ethoxylate groups were obtained with hydrophobic chain lengths of eight and twelve carbon atoms. The average slope from these two trends was computed to predict the effect of the number of ethoxylate groups on  $\log P_{\text{ow}}$ . In addition, two of the surfactants had five ethoxylate units with differing carbon chain lengths and three of the surfactants had eight ethoxylate units with different carbon chain lengths. The average slope from these two sets of data was used to determine the effect of carbon chain length on  $\log P_{\text{ow}}$ . These two slopes were then used to calculate an arbitrary constant so the data

from surfactants not included in the above mentioned series could also be used. This arbitrary constant ( $C_{AES}$ ) is defined as:

$$C_{AES} = 0.62 \cdot N_C - 0.24 \cdot N_{EO} \dots \dots \dots \text{Eq. 1}$$

where  $N_C$  is the number of carbon atoms in the hydrophobic chain,  $N_{EO}$  is the number of ethoxylate units on each surfactant molecule, 0.62 is the average slope (Fig. 1) in the  $\log P_{ow}$  versus carbon chain plots, and -0.24 is the average slope in the  $\log P_{ow}$  versus the number of ethoxylate groups plots (Fig. 1). This constant was calculated for each surfactant and plotted against its experimentally measured  $\log P_{ow}$ , shown in Fig. 2. Included in this plot are  $\log P_{ow}$  data from the surfactants with different numbers of ethoxylate groups and carbon chain lengths from all other surfactants studied whose data were not used to define  $C_{AES}$ . As is shown below, these data points fall in line with the other  $C_{AES}$  data. The resulting straight line now allows one to predict reasonable  $\log P_{ow}$  values for AES not included in this study using Equation 2.

$$\log P_{ow} = 1.047 \cdot C_{AES} - 1.475 \dots \dots \dots \text{Eq. 2}$$

Equation 2 was used to calculate the  $\log P_{ow}$  for each of the surfactants studied to compare with the experimentally measured values. The maximum span between the calculated values and experimental values was 0.12 log units and well within the accepted variance of 0.3 log units. This data is shown in Table 2.

## Industrial Surfactants

In previous work, the  $\log P_{ow}$  for an industrial AES was experimentally determined using the method described here (8). The surfactant consisted of three different carbon chain lengths with an ethoxylate distribution ranging from 1–15 ethoxylate groups resulting in nearly 50 individual molecules. In such complicated samples, separating each individual surfactant molecule in any significant quantity can be tedious. Instead, a C18 column was used to separate the surfactants according to their hydrophobic chain length. Three  $\log P_{ow}$  values were then calculated, one for each carbon chain length.

Using the MS data from these studies, each individual ion was extracted and the relative abundance of each individual molecule was determined. The relative abundance of each surfactant molecule and the  $\log P_{ow}$  values predicted in the current study were then used to predict the relative number of surfactant molecules in both the n-octanol and water layers. The total number of molecules for each carbon chain distribution in both the n-octanol and water layer was then determined. From these values,  $\log P_{ow}$  values for the three carbon chain distributions in the industrial sample were predicted. As is shown in Table 5, the predicted values are within the accepted 0.3 log unit variance.

## CONCLUSIONS

There are very few  $\log P_{ow}$  values reported for surfactants in literature. However, in this work we have shown that true partition coefficients can be determined for pure surfactants. Until now, measuring  $\log P_{ow}$  values for industrial surfactants presented a challenge. It has been demonstrated that partition coefficients for industrial surfactants composed of many individual molecules can be predicted using experimental data obtained from other structurally similar surfactants. The calculated  $\log P_{ow}$  values reported in this study for an industrial surfactant are within the accepted margin of error of experimental data previously obtained.

While experimentally measuring the partition coefficient for surfactant blends can be difficult, determining the  $\log P_{ow}$  for pure surfactants is reasonably simple if a few precautions are taken. Data obtained from analysis of pure surfactants can be used to predict partition coefficients for similar surfactants that are not commercially available in the pure state but are relatively common in industrial surfactants. The objective of this study is to allow one to predict partition coefficients for complex surfactant blends and eliminate the need for oftentimes difficult separation and detection techniques required when such complex samples are involved.

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**Table 1.** LC-MS parameters used for the determination of surfactant in water and octanol layers.

Surfactant	Flow Rate, ml/min	Injection Volume Water, $\mu\text{l}$	Injection Volume Octanol, $\mu\text{l}$	Ion Detected, $m+18/z$
$\text{C}_6\text{EO}_5$	0.5	5	5	340
$\text{C}_8\text{EO}_3$	0.5	5	5	280
$\text{C}_8\text{EO}_4$	0.5	5	5	324
$\text{C}_8\text{EO}_5$	0.5	5	5	368
$\text{C}_{10}\text{EO}_8$	0.5	5	5	528
$\text{C}_{12}\text{EO}_6$	0.8	20	5	468
$\text{C}_{12}\text{EO}_7$	0.8	20	5	512
$\text{C}_{12}\text{EO}_8$	0.8	20	20	556
$\text{C}_{14}\text{EO}_8$	0.8	20	20	584

**Table 2.** The maximum percentage of surfactant molecules in each slow-stir sample that may be located at the octanol/water interface is shown to be a small fraction of the total number of molecules.

Surfactant	Area Per Molecule, $\text{\AA}^2*$	Volume Water, l	Concentration, M	Molecules at the Interface, %
$\text{C}_6\text{EO}_5$	50	0.225	$1.58 \times 10^{-5}$	0.058
$\text{C}_8\text{EO}_3$	36	0.225	$9.15 \times 10^{-7}$	0.065
$\text{C}_8\text{EO}_4$	44	0.225	$4.11 \times 10^{-8}$	1.399
$\text{C}_8\text{EO}_5$	50	0.225	$4.88 \times 10^{-8}$	1.929
$\text{C}_{10}\text{EO}_8$	62	0.225	$1.49 \times 10^{-8}$	1.071
$\text{C}_{12}\text{EO}_6$	55	0.225	$2.66 \times 10^{-9}$	0.137
$\text{C}_{12}\text{EO}_7$	55**	0.225	$3.44 \times 10^{-9}$	0.181
$\text{C}_{12}\text{EO}_8$	62	0.225	$1.46 \times 10^{-7}$	0.016
$\text{C}_{14}\text{EO}_8$	62	0.225	$8.65 \times 10^{-9}$	0.010

\*Values were obtained from Table 10 in the work of Lu, Thomas, and Penfold (24).

\*\*These values were extrapolated from the data presented by Lu and coworkers.

**Table 3.** The  $\log P_{ow}$  and percent recoveries for the 16 surfactants tested in this study.

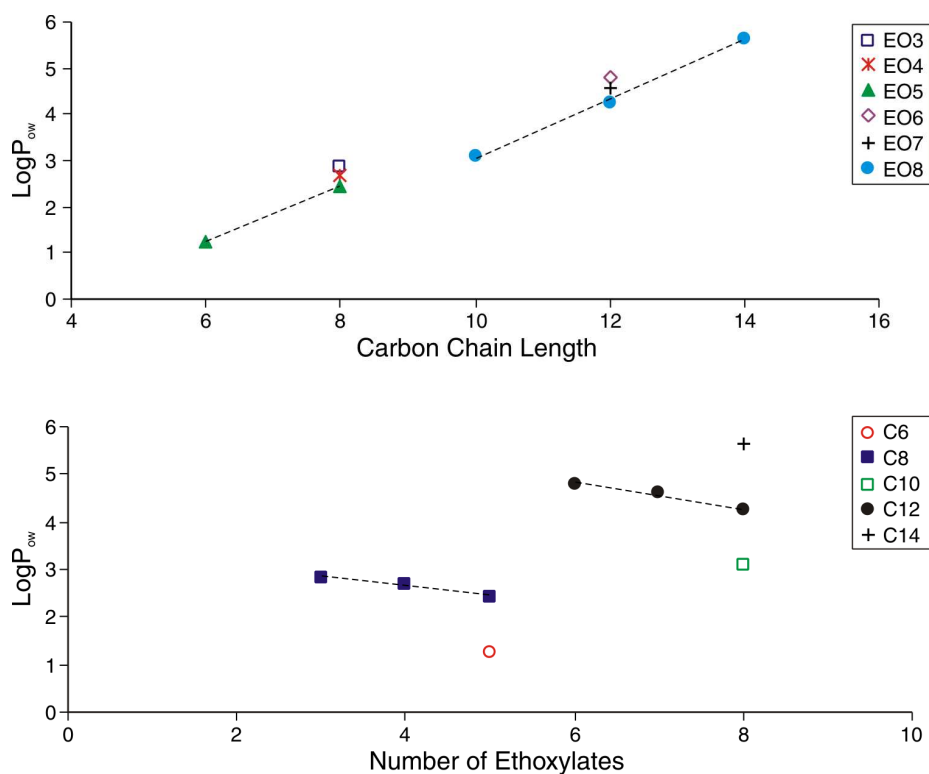
Surfactant	$\log P_{ow}$	Percent Recovery
$\text{C}_6\text{EO}_5$	$1.24 \pm 0.03$	$89\% \pm 2.8$
$\text{C}_8\text{EO}_3$	$2.84 \pm 0.02$	$71\% \pm 2.4$
$\text{C}_8\text{EO}_4$	$2.68 \pm 0.09$	$80\% \pm 4.5$
$\text{C}_8\text{EO}_5$	$2.43 \pm 0.03$	$75\% \pm 4.6$
$\text{C}_{10}\text{EO}_8$	$3.09 \pm 0.03$	$76\% \pm 5.2$
$\text{C}_{12}\text{EO}_6$	$4.81 \pm 0.09$	$85\% \pm 5.4$
$\text{C}_{12}\text{EO}_7$	$4.59 \pm 0.04$	$82\% \pm 6.4$
$\text{C}_{12}\text{EO}_8$	$4.25 \pm 0.08$	$94\% \pm 15.8$
$\text{C}_{14}\text{EO}_8$	$5.65 \pm 0.03$	$81\% \pm 11.3$

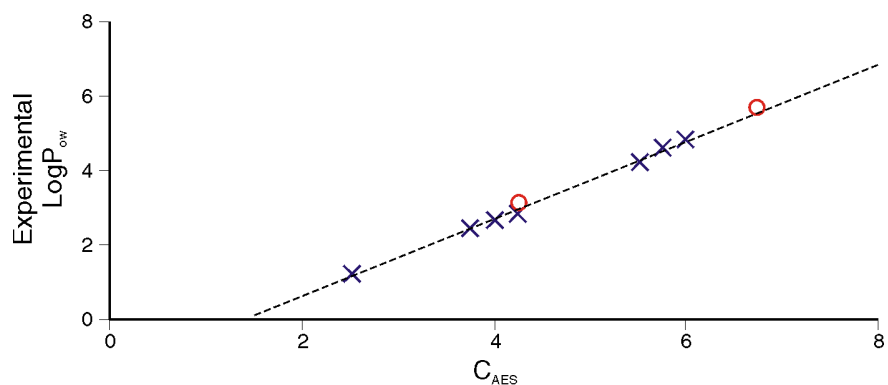
**Table 4.** Experimental and predicted  $\log P_{ow}$  values.

$N_c$	$N_{EO}$	Experimental $\log P_{ow}$	$C_{AES}$	Predicted $\log P_{ow}$	Difference
6	5	<b>1.24</b>	2.52	<b>1.16</b>	0.08
8	3	<b>2.84</b>	4.24	<b>2.96</b>	0.12
8	4	<b>2.68</b>	4	<b>2.71</b>	0.03
8	5	<b>2.43</b>	3.76	<b>2.46</b>	0.03
10	8	<b>3.09</b>	4.28	<b>3.01</b>	0.08
12	6	<b>4.81</b>	6	<b>4.81</b>	0.00
12	7	<b>4.59</b>	5.76	<b>4.56</b>	0.03
12	8	<b>4.25</b>	5.52	<b>4.30</b>	0.05
14	8	<b>5.65</b>	6.76	<b>5.60</b>	0.05

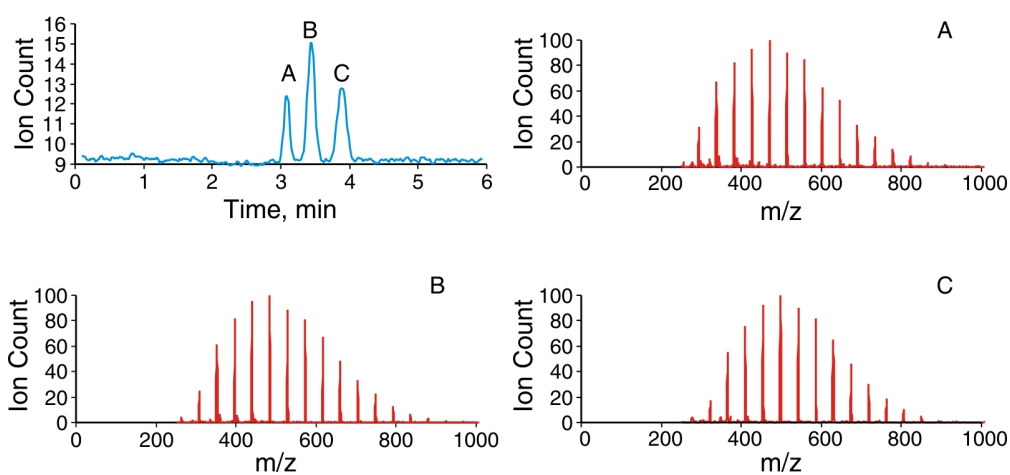
**Table 5.** Experimental and predicted  $\log P_{ow}$  values for an industrial alkyl ethoxylate surfactant (8).

Component	A	B	C
Experimental $\log P_{ow}$ <sup>8</sup>	2.16	2.66	3.27
Predicted $\log P_{ow}$	1.87	2.50	3.17
Difference	0.29	0.16	0.10
Difference, %	13.5	5.93	2.95

**Figure 1.** Effect of carbon chain length (above) and the number of ethoxylate groups (below) on the  $\log P_{ow}$  for AES.



**Figure 2.** Experimental  $\log P_{ow}$  plotted versus the arbitrary constant  $C_{AES}$  for all surfactants studied. Data used to define  $C_{AES}$  are marked by x's and data that was not used to define this constant are marked by circles.



**Figure 3.** LC-MS chromatogram of an industrial AES (A) and the mass spectra corresponding to the peaks with elution times of 3.2 (B), 3.6 (C), and 4.1 minutes (D). Conditions:  $m/z$  205–1,200; flow rate, 0.5 ml/min; eluent, 95% acetonitrile/5% 0.1 M; ammonium formate, concentration, 1 mg/l.