# The Monolayer Structure of the Branched Nonyl Phenol Oxyethylene Glycols at the Air–Water Interface

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The structure of the monolayers formed by a group of monodisperse nonyl phenol ethoxylates with parasubstituted 1-butylpentyl chains (*para*-(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>(OC<sub>2</sub>H<sub>4</sub>)<sub>n</sub>OH, abbreviated to BNPE<sub>n</sub>, n = 4, 8, and 12) at the air-water interface has been determined by surface tension measurements and neutron reflection. The critical micellar concentration (cmc) was found to be  $1.1 \pm 0.3 \times 10^{-5}$  M for BNPE<sub>4</sub>,  $4.0 \pm 0.3 \times 10^{-5}$ M for BNPE<sub>8</sub> and  $8.0 \pm 0.3 \times 10^{-5}$  M for BNPE<sub>12</sub> and the limiting area per molecule ( $A_{cmc}$ ) at the cmc to be  $46 \pm 3$ ,  $61 \pm 4$ , and  $75 \pm 5$  Å<sup>2</sup>, respectively. The values of  $A_{cmc}$  are almost identical to those obtained from dodecyl ethoxylates ( $C_{12}E_n$ ) for the same size of the headgroups, suggesting that  $A_{cmc}$  for these nonionic surfactants is determined by the size of the headgroups and is not affected by the chemical structure of the hydrophobic chains. The thicknesses of the nonyl phenol layers projected onto the surface normal direction were found to be  $18 \pm 3$  Å for BNPE<sub>4</sub>,  $19 \pm 3$  Å for BNPE<sub>8</sub>, and  $22 \pm 3$  Å for BNPE<sub>12</sub>. In all cases they were about twice as thick as the fully extended chain, suggesting a broad distribution of the hydrophobic chain across the layer and hence a strong mixing of the chain with the ethoxylate groups.

#### Introduction

Alkyl phenol ethoxylates (APEs) have been widely used in various domestic and industrial applications, ranging from heavy duty detergents and car shampoos to stabilizers for colloidal dispersions. APEs are also used in many biological processes to mediate the activities of proteins and enzymes. Unlike sodium dodecyl sulfate (SDS), APE surfactants are mild and their binding to many globular proteins does not usually cause the breakdown of the globular framework.<sup>1</sup> However, APEs are effective in deactivating a number of biological molecules such as cytochrome oxidase, adenylate cyclase.<sup>2,3</sup> These properties are thought to be related to the specific binding of APE molecules to the active sites of these biological molecules. Such selective binding is in sharp contrast to the cooperative mode of interaction between protein and ionic surfactants such as SDS, which usually deteriorate the native or near-native structures.

Many investigations have been made to characterize the adsorption and aggregation of APE surfactants in aqueous solutions using surface tension measurements, NMR and dynamic light scattering.<sup>4–12</sup> These studies have demonstrated how the critical micellar concentration (cmc), surface and interfacial tension, the size and shape of surfactant aggregates, and cloud points are affected by temperature, salt type and concentration, and the size of ethoxylate headgroups. The main drawback in these studies is that impure samples have been used. For most commercial APE samples, the alkyl chains vary in the number of carbons as well as in the degree of branching and the ethoxylate groups are polydisperse. For example, Triton X-100 has a nominal chemical formula of

 $C_8H_{17}C_6H_4(OC_2H_4)_{9-10}OH$ . Our NMR measurements suggest that the octyl chain has at least four different alkyl chain structures and liquid chromatography shows that the length of the ethoxylate headgroups is highly polydisperse. The polydispersity in these surfactant samples has undermined the reliability of many results of such studies reported in the literature. In some cases, the uncertainty in the chemical structure of the surfactant samples also constrains the interpretation of the data.<sup>5,6,9</sup>

In a systematic investigation of the adsorption of nonionic surfactants, we have recently studied the structural conformation of alkyl ethoxylates  $C_{12}E_n$  at the air-water interface using neutron reflection. We found that for this series of surfactants a strong mixing exists between the alkyl chains and the ethoxylate headgroups.<sup>13–17</sup> The extent of mixing increases with the size of the headgroups. In an effort to examine the effect of the chemical structure of the alkyl chain on the conformational structure of the adsorbed monolayers we have recently studied the adsorption of alkyl phenol ethoxylates  $(C_mH_{2m+1}C_6H_4$ - $(OC_2H_4)_nOH)$  at the air-water interface using neutron reflection combined with surface tension measurements. Pure monodisperse APE samples have been used throughout this work. The results from this study together with those of  $C_m E_n$  series will allow a direct comparison to be made between the chemical configuration of the hydrophobic groups and the structure of the adsorbed nonionic surfactant layers.

Most existing synthetic routes for making APE samples utilize AlCl<sub>3</sub> or ZnCl<sub>2</sub> as an alkylation catalyst, which causes a random branching of the alkyl chain and substitution at both para and ortho positions.<sup>18</sup> We have hence devised new synthetic routes so that only one isomeric structure is obtained in a given synthesis. We have prepared monodisperse para and ortho nonyl

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$$C_4H_9$$
  
 $C_4H_9$   
 $C_4H_9$   
 $O(C_2H_4O)_nH$   
 $C_4D_9$   
 $O(C_2H_4O)_nH$ 

**Figure 1.** Molecular configuration of the branched nonyl phenol ethoxylates with n = 4, 8, and 12 and with the alkyl chains hydrogenated and deuterated.

phenol ethoxylates in fully hydrogenated and alkyl chain deuterated forms. In this work we present the results on the surface behavior of the para-substituted nonyl phenol ethoxylates with branched nonyl chains at the air—water interface. Our main aim is to examine how the branching in the alkyl chain and the insertion of a benzyl ring in the alkyl chain affect the monolayer structure of the nonionic surfactant. The measurements recorded in this paper have been made using a series of BNPE samples with different ethoxylate headgroups.

#### **Experimental Section**

Two isotopic species of the surfactants were synthesized,  $para-C_9H_{19}C_6H_4(OC_2H_4)_nOH$ , abbreviated to h-BNPE<sub>n</sub>, n = 4, 8, and 12, and  $para-C_8D_{17}CH_2C_6H_4(OC_2H_4)_nOH$ , abbreviated to d-BNPE<sub>n</sub>, n = 4, 8, and 12. The chemical structure of the two labeled species is shown in Figure 1. The main reaction steps are outlined as follows:

$$p-\text{CHOC}_{6}\text{H}_{4}\text{OCH}_{3} \xrightarrow{2C_{4}\text{H}_{9}\text{MgBr}} p-(C_{4}\text{H}_{9})_{2}\text{COHC}_{6}\text{H}_{4}\text{OCH}_{3} (1)$$

$$\xrightarrow{\text{NaBH}_{4}/\text{CF}_{3}\text{COOH}} p-(C_{4}\text{H}_{9})_{2}\text{CHC}_{6}\text{H}_{4}\text{OCH}_{3} \xrightarrow{\text{BBr}_{3}} p-(C_{4}\text{H}_{9})_{2}\text{CHC}_{6}\text{H}_{4}\text{OH}$$

$$\xrightarrow{\text{TsCI/C}_{2}\text{H}_{5})_{3}\text{N}} p-(C_{4}\text{H}_{9})_{2}\text{CHC}_{6}\text{H}_{4}\text{OTs}$$

$$\xrightarrow{\text{K+O-(C}_{2}\text{H}_{4}\text{O})_{4}\text{H}} p-(C_{4}\text{H}_{9})_{2}\text{CHC}_{6}\text{H}_{4}(\text{OC}_{2}\text{H}_{4})_{4}\text{OH}$$

A Grignard reaction coupled bromobutane and 4-methoxybenzylaldehyde to afford a tertiary alcohol. Reduction of the hydroxyl group with sodium borohydride in trifluoro acetic acid, followed by deprotection of the latent phenol functionality with boron tribromide, gave branched chain nonyl phenol an overall 40% yield. After purification by flash column chromatography the tosylate of the phenol was formed by reaction with paratoluenesulfonyl chloride (abbreviated to Ts) in the presence of triethylamine using dichloromethane as solvent. In a separate flask, potassium tert-butoxide (twice in excess of phenol in molar ratio) was reacted with dry tetraethylene glycol (six times in excess of phenol) to form the mono potassium salt. The tertbutyl alcohol released was removed under vacuum. The tosylated phenol was then added to the monopotassium salt of tetraethylene glycol and with vigorous stirring the reaction mixture maintained 80 °C under vacuum for 4 h. The reaction mixture was neutralized using concentrated hydrochloric acid, and was then extracted several times with diethyl ether, followed by a concentration of the combined organic extracts and flash column chromatography to give BNPE4 in a 40% yield to the starting phenol. BNPE8 was prepared by coupling BNPE4 with tetraethylene glycol in a similar manner, and BNPE<sub>12</sub> was then prepared by a repeated coupling of BNPE<sub>8</sub> with tetraethylene glycol.

Alkyl chain deuterated samples were made using the same procedure, except the starting Grignard reagent was made from

deuterated bromobutane. Proton NMR spectra have been taken for all the samples and Figure 2 shows the result for BNPE<sub>4</sub> as an example. Within the spectrum the ratios between different protons follow the stoichiometric relation within the experimental resolution. The peak at 0.8 ppm corresponds to  $-CH_3$ , around 1.2 ppm to the middle  $-(CH_2 CH_2)$ , at 1.5 ppm to the end  $-CH_2-$  on the butyl chain, at 2.4 ppm to the single H on the tert carbon at the end of the two butyl chains, the three peaks around 4 ppm to the whole oxyethylene units, and the two peaks at 6.8 and 7 ppm to the phenol ring. The peak at 7.3 ppm arises from the deuterium chloroform and the small one at 2.7 ppm may originate from the labile OH group. The two small ones around 2 ppm are possibly associated with traces of ethyl ether remaining in the sample or other unknown impurities. In the case of  $BNPE_8$  and  $BNPE_{12}$ , the positions of the peaks are almost identical and the only changes are the integrated areas for the headgroups around 4 ppm that increase in proportion to *n*, as expected. <sup>1</sup>H NMR spectra have also been taken for the alkyl chain deuterated samples and the integrated areas below 2 ppm (corresponding to the residual protons in the butyl groups) allow a direct determination of the degree of deuteration. The level of deuteration in the butyl groups was found to be 92  $\pm$ 2%. Bromobutane (99% pure) and 4-methoxybenzylaldehyde (98% pure) were obtained from Aldrich. Deuterated bromobutane was made by brominating deuterated butanol (BOSTI, Moscow) following the procedures given in ref 18.

The neutron reflection measurements were done on the white beam time-of-flight reflectometer SURF at the Rutherford Appleton Laboratory, ISIS, Didcot, UK.19 To avoid mechanical vibration, the sample holder was mounted on an anti-vibration table. Positive liquid meniscus was obtained by pouring surfactant solutions into Teflon troughs. The position of each liquid surface was aligned using a laser beam that shares the same beam path as neutron radiation. Neutron beam intensities were calibrated with respect to the reflectivity from a D<sub>2</sub>O surface. A flat background determined by extrapolation to the high values of momentum transfer,  $\kappa$  ( $\kappa = (4\pi \sin \theta)/\lambda$ ), where  $\lambda$  is the wavelength and  $\theta$  is the glancing angle of incidence, was subtracted. All the experiments were performed at  $25 \pm 2$  °C. Ultrapure water was used for all the measurements (Elga Ultrapure) and all the glassware and Teflon troughs for the reflection measurements were cleaned using alkaline detergent (Decon 90) followed by repeated washing in ultrapure water. Surface tension measurements were made using a Kruss K10 maximum pull tensiometer with a Pt du Nouy ring. For a given concentration several readings were typically taken and the difference between the repeated measurements was usually less than 0.5 mN m<sup>-1</sup> near the cmc and was about 1 mN m<sup>-1</sup> over the dilute concentration region.

#### **Results and Discussion**

A. Surface Tension Measurements. The cmc for the nonyl phenol ethoxylates was determined by surface tension measurements. Figure 3 shows the variation of surface tension with log [concentration] for the fully hydrogenated surfactants. The reading of surface tension was found to vary with time for all the nonionic surfactants studied in this work. It typically took about 5-10 min for the adsorption to reach a constant value at the concentration around the cmc, while over the dilute concentration range, it took some 30 min for the saturated adsorption to be reached. Time-dependent adsorption for this type of surfactants was also observed by Crook et al.<sup>4</sup> and Schick et al.<sup>5</sup> Our observed time scale for reaching constant surface tension values is broadly consistent with that reported by these

45

ppm





Figure 3. Surface tension plots for the branched nonyl phenol ethoxylates with the number of the ethoxylate units equal to 4 ( $\triangle$ ), 8 (+), and 12  $(\bullet)$ . The dashed lines are the limiting slopes at the cmc converted from the surface excesses determined from neutron reflection.

authors. The results shown in Figure 3 are the equilibrated values. The absence of a minimum around the cmc in each tension curve is consistent with the samples prepared being of high purity. The cmc was found to be  $(1.1 \pm 0.3) \times 10^{-5}$  M for h-BNPE4, (4.0  $\pm$  0.3)  $\times$   $10^{-5}$  M for h-BNPE8 and (8.0  $\pm$ 0.3)  $\times 10^{-5}$  M for h-BNPE<sub>12</sub>. The surface tension plots for the corresponding chain deuterated surfactants were found to be identical to the hydrogenated ones, within an error margin of 1 mN m<sup>-1</sup>. The agreement was better in the region of the cmc, suggesting that both deuterated and hydrogenated surfactants were of similar purity. There was no observable difference in the surface activity, caused by either the traces of impurities or the possible difference in surface activity arising from the deuterium labeling.

We have previously shown that analysis of the surface tension data below the cmc using the Gibbs equation leads to a reliable estimate of surface excess (the adsorbed amount) at different bulk surfactant concentrations,<sup>13,15</sup> provided that measurements are made over a sufficiently wide range of surfactant concentration to ensure that accurate slopes are obtained. For the surfactants studied in this work, the cmc is relatively low and when the bulk concentration is below 5  $\times$  10<sup>-6</sup> M the reproducibility in the tension measurement was found to be poor. The surface tension data are thus not accurate enough to render a reliable derivation of the variation of surface excess with bulk



**Figure 4.** Plots of log[cmc] versus n for OPE<sub>n</sub> (O),  $C_{12}E_n$  ( $\Delta$ ), and  $BNPE_n$  (+). The straight lines through each set of data are the best fits.

concentration under these conditions. Nevertheless, the limiting values of surface excess ( $\Gamma_{cmc}$ ) for these surfactants can still be estimated from the tension plots by taking the limiting slopes just below the cmc. These values can then be directly compared with the surface excesses obtained from neutron reflection. The dashed lines shown in Figure 3 represent the neutron surface excesses measured at the cmc for each of the surfactants. These straight lines are in reasonable agreement with the limiting slopes of the surface tension plots at the cmc, suggesting that the surface excesses from both surface tension measurements and neutron reflection are in a reasonably good agreement.

There are no cmc values for these surfactants in the literature for comparison. It is, however, useful to note that Crook et al.<sup>4</sup> have measured surface tension for a series of pure octyl phenol ethoxylates (abbreviated to  $OPE_n$ ) and the commercial Triton series at the air-water and oil-water interfaces. Comparison of our data with the results from their pure para-substituted  $OPE_n$ will enable us to examine both the effect of the number of carbons in the alkyl chain (m) and the effect of the length of ethoxylate groups (n) on the cmc. Both sets of alkyl phenol results are shown in Figure 4. It can be seen from Figure 4 that an increase in m by one has resulted in the decrease of the cmc by almost a factor of 10. This trend is consistent for all the surfactants studied with different sizes of ethoxylate headgroups. Klevens<sup>20</sup> has shown that for many surfactants containing straight alkyl chains as their hydrophobic groups, the variation

of the cmc with the length of the alkyl chain follows a half logarithmic relation: that is, log[cmc] decreases linearly with m. Meguro et al.<sup>21</sup> have examined the cmc variation of the  $C_m E_n$ series with the alkyl chain length and found that the slope of the plot of  $\log[\text{cmc}]$  versus m is about -0.5, suggesting that with an increase of one carbon in the alkyl chain, the cmc is also decreased by a factor of 10, an observation consistent with that from the alkyl phenol surfactants. It should, however, be noted that for most of the straight chain ionic surfactants the slope was found to be around -0.3, showing that an increase of one carbon decreases the cmc by a factor of 5.<sup>22</sup> Because the dependence of the cmc on the number of carbons in the hydrophobic group is the same for  $C_m E_n$ ,  $OPE_n$ , and  $BNPE_n$ , the results thus suggest that the inclusion of the phenol group does not alter the rate of decrease of the cmc on the number of carbons in the hydrophobic chain. It is also interesting to mention that while the alkyl chain in  $C_m E_n$  is straight, the alkyl chains in APE samples are branched, and the branching between the  $OPE_m$  and  $NPE_m$  surfactants is different. Such differences do not appear to affect the rate of variation of the cmc on m either.

The dependence of the cmc on the size of the hydrophilic headgroups for nonionic surfactants has also been discussed in the literature.<sup>22,23</sup> An empirical linear relationship between log-[cmc] and n has also been proposed, but the slope of the plot in this case is positive and is much smaller than the absolute value corresponding to the plot of log[cmc] versus m, showing that the increase of cmc with n is much slower than its decrease with *m*. The fact that two sets of the data for  $BNPE_n$  and  $OPE_n$ in Figure 4 can be approximated to two parallel straight lines suggests that the proposed linear relation holds and the difference in the branching of alkyl chains does not affect the dependence of the cmc on n. The slope of the two lines was found to be about 0.10. For comparison, the variation of the cmc for  $C_{12}E_n$  series is also shown in Figure 4 and the slope of the best linear fit to the data was found to be 0.03, showing that the cmc for APE series increases 3 times faster with n than that for the  $C_m E_n$  series. However, it should be noted that both Hsiao et al.<sup>24</sup> and Crook et al.<sup>4</sup> have shown that the linear relation for APE series only holds when n is less than 10, beyond which the rate of increase in cmc with n tends to slow. This trend is almost visible in Figure 4 in that the data do not exactly follow a linear relation with n.

**B.** Surface Excess from Neutron Reflection. The surface excess can be determined more reliably in neutron reflection and the principle can be outlined as follows.

In a neutron reflection experiment the intensity of the incoming beam ( $I_0$ ) and that of the exiting beam (I) are measured and the ratio of  $I/I_0$  is known as neutron reflectivity ( $R(\kappa)$ ). In a specular reflection  $R(\kappa)$  is a function of the scattering length density distribution ( $\rho(z)$ ) normal to the interface,<sup>25,26</sup> which depends on the number densities of each atom species  $n_i$  and their known scattering lengths  $b_i$ :

$$\rho = \sum n_i b_i \tag{2}$$

Since the value of  $b_i$  varies from isotope to isotope, the use of isotopic labeling can alter neutron reflectivity for a given chemical structure. For a hydrocarbon system, the most straightforward application is the substitution of hydrogen by deuterium. Since the scattering lengths of D and H are of opposite sign, the scattering length density of water can be varied over a wide range. For example, if one mole of D<sub>2</sub>O is mixed with 11 mol of H<sub>2</sub>O, the mixed water will have zero scattering length. When neutron reflection is performed at the air—water interface no



**Figure 5.** Surface excess plots for the branched nonyl phenol ethoxylates with n = 4 ( $\bullet$ ), 8 (+), and 12 ( $\triangle$ ). The arrows indicate the cmc and the solid lines are to guide the eye.

specular reflectivity will arise from the interface. This mixed water is usually termed null reflecting water (NRW). When a deuterated surfactant is adsorbed on the surface of NRW, the surfactant is the only species that contributes to the specular reflectivity. Under these conditions, and if the adsorbed layer is assumed to be uniform, the area per molecule *A* is given by

$$A = \frac{\sum m_i b_i}{\rho \tau} \tag{3}$$

where  $m_i$  is the number of *i*th atom with scattering length  $b_i$  and  $\tau$  is the thickness of the layer. The relationship between *A* and surface excess  $\Gamma$  is

$$\Gamma = \frac{1}{AN_a} \tag{4}$$

where  $N_a$  is the Avogadro's constant. In fitting the reflectivity profiles with a uniform layer model, it is usually found that  $\tau$ and  $\rho$  can be varied over a limited range, but the variations cancel in their contribution to A so that A is to a good approximation independent of the assumption that the layer is uniform.

The surface excesses for  $BNPE_n$  have been obtained by performing neutron reflectivity measurements using the alkyl chain deuterated surfactants in NRW. Figure 5 shows the resulting surface excesses as a function of bulk surfactant concentration in NRW at 25 °C. The arrows in Figure 5 mark the cmc for each of the surfactants. An interesting feature of Figure 5 is that the change of surface excess with concentration becomes more gradual as n increases. The same trend has been observed for the monodisperse  $C_{12}E_n$  series.<sup>17</sup> The slower variation of surface coverage and surface tension with bulk concentrations of BNPE<sub>n</sub> and  $C_{12}E_n$  at large values of n resembles the behavior of poly(ethylene oxide) (PEO),27 suggesting that as the size of the headgroups increases the effect of the hydrophobic groups becomes less significant. A further interesting feature is that the limiting surface excess above the cmc decreases with n, showing that the limiting area per molecule increases with the size of the headgroups.  $A_{\rm cmc}$  was



**Figure 6.** Neutron reflectivity profiles for the alkyl chain deuterated nonyl phenol ethoxylates in NRW with n = 4 ( $\oplus$ ), 8 (+), and 12 ( $\triangle$ ). The continuous lines are calculated using uniform layer model and the structural parameters are given in Table 2.

found to be  $46 \pm 3 \text{ Å}^2$  for BNPE<sub>4</sub> as compared with  $44 \pm 3 \text{ Å}^2$  for C<sub>12</sub>E<sub>4</sub>,  $61 \pm 4 \text{ Å}^2$  for BNPE<sub>8</sub> as compared with  $62 \pm 3 \text{ Å}^2$  for C<sub>12</sub>E<sub>8</sub>,  $75 \pm 5 \text{ Å}^2$  for BNPE<sub>12</sub> as compared with  $72 \pm 5 \text{ Å}^2$  for C<sub>12</sub>E<sub>12</sub>. The almost identical  $A_{\rm cmc}$  obtained for the same size of the ethoxylate headgroups suggests that the change in the structure of the hydrophobic chain in the form of the alkyl chain branching and the insertion of the benzyl chain has negligible effect on the limiting area per molecule.  $A_{\rm cmc}$  must be predominantly determined by the size of the ethoxylate headgroups.

**C. Structure Determination.** Although the difference in the chemical configuration of the hydrophobic chains does not affect the limiting area per molecule at the cmc, it is interesting to examine if such difference affects the distributions of different fragments within the adsorbed layers. For each surfactant studied in this work, reflectivity profiles were measured under three different isotopic contrasts: the alkyl chain deuterated in NRW and in D<sub>2</sub>O, and the fully hydrogenated in D<sub>2</sub>O. These measurements allow the determination of the distributions of the hydrophobic groups and their locations relative to the water across the interface. Although these measurements do not include the use of headgroup deuterated surfactants, some useful information about the distributions of the ethoxylate headgroups can still be gained, as will be discussed later.

Neutron reflectivity is often analyzed using the optical matrix method.<sup>28</sup> The procedure for extracting structural information is through model fitting to the different reflectivity profiles. A structural model is usually assumed for an interface and its corresponding reflectivity is then calculated using the optical matrix formula. The calculated reflectivity is then compared with the measured one and the structural parameters are modified in a least-squares criterion until a good fit is obtained. The parameters directly used in the calculation are mainly the thicknesses of the layers  $\tau$  and the corresponding scattering length densities  $\rho$ , from which A and  $\Gamma$  can be obtained through eqs 3 and 4. Figure 6 shows the best fits to the measured reflectivity profiles at the cmc for the three alkyl chain deuterated surfactants in NRW assuming uniform layer distributions. The scattering lengths and volumes for different fragments used in the fitting are given in Table 1 and the resultant structural

TABLE 1: Physical Constants Used in Data Analysis<sup>a</sup>

fragment	$\Sigma b_i  imes 10^{5}$ /Å	volume/Å3	$ ho  imes 10^6/{ m \AA}^{-2}$	$l_{\rm c}$
(C <sub>4</sub> D <sub>9</sub> ) <sub>2</sub> CH-	161.2(92%D)	265	6.1	7.8
$(C_4H_9)_2CH -$	-11.2	265	-0.4	7.8
$-C_6H_4-$	24.9	160	1.6	3
$-(OC_2H_4)_4OH$	19.4	260	0.75	15.5
$-(OC_2H_4)_8OH$	35.9	510	0.7	30
$-(OC_2H_4)_{12}OH$	52.5	760	0.7	44
H <sub>2</sub> O	-1.68	30	-0.56	
$D_2O$	19.1	30	6.35	

<sup>*a*</sup> The values of scattering lengths were from ref 33; the fragment volumes and fully extended lengths were from refs 34 and 35;  $l_c$  denotes the fully extended length.

 
 TABLE 2: Structural Parameters for BNPE<sub>m</sub> Obtained from Uniform Layer Model Fitting<sup>a</sup>

isotope	$A/{ m \AA}^2$	$\tau(\sigma'_{\rm c}) \pm 2/{\rm \AA}$	п
d-BNPE <sub>4</sub> /NRW	$46 \pm 3$	22(20)	-
d-BNPE <sub>4</sub> /D <sub>2</sub> O	$46 \pm 3$	23	$7 \pm 1$
h-BNPE <sub>4</sub> /D <sub>2</sub> O	$46 \pm 3$	12.5	$7 \pm 1$
d-BNPE <sub>8</sub> /NRW	$62 \pm 4$	24(22)	-
d-BNPE <sub>8</sub> /D <sub>2</sub> O	$61 \pm 4$	25.5	$16 \pm 1$
h-BNPE <sub>8</sub> /D <sub>2</sub> O	$61 \pm 4$	17	$16 \pm 1$
d-BNPE <sub>12</sub> /NRW	$73 \pm 5$	27(24)	-
d-BNPE <sub>12</sub> /D <sub>2</sub> O	$76 \pm 5$	28	$24 \pm 2$
h-BNPE <sub>12</sub> /D <sub>2</sub> O	$75\pm5$	21	$24 \pm 2$

a n denotes the number of water molecules required to give appropriate scattering length density to fit the reflectivity profile at a given isotopic substitution.

parameters are listed in Table 2. The calculated reflectivity profiles fit all the three measured ones well within the experimental error, suggesting that the uniform layer model is a reasonable approximation for describing the distributions of the layers in NRW. The fitting to the reflectivity profiles shown in Figure 6 gives the thicknesses of  $22 \pm 3$  Å for BNPE<sub>4</sub>,  $24 \pm 3$  Å for BNPE<sub>8</sub>, and  $27 \pm 3$  Å for BNPE<sub>12</sub>. Since the scattering length from the hydrogenated ethoxylate groups is relatively small, the thicknesses obtained mainly represent the distributions of the nonyl phenol groups with a small fractional contribution from ethoxylate headgroups.

Although the hydrogenated ethoxylate groups in NRW are hardly visible, the situation is different if the measurement is made in D<sub>2</sub>O. The association of D<sub>2</sub>O molecules with the ethoxylate groups serves to highlight the distributions of the headgroups. Since the scattering length density for one ethoxylate unit is close to zero (see Table 1) and its volume is equivalent to two water molecules, the association of two D<sub>2</sub>O molecules to each ethoxylate unit will produce an average scattering length density that is about half of the value for the pure D<sub>2</sub>O. When a fully hydrogenated surfactant is adsorbed at the surface of D<sub>2</sub>O, the region above water will have an average scattering length density close to zero and is virtually invisible. The measurement with this contrast offers reliable information about the distribution of the ethoxylate groups. Figure 7 shows the measured reflectivity profiles for the fully hydrogenated surfactants in D<sub>2</sub>O. The reflectivity from the surface of pure D<sub>2</sub>O is also shown (dashed line) for comparison. The large difference between the water profile and those in the presence of fully hydrogenated surfactants shows that the measurement in D<sub>2</sub>O is quite sensitive to the distributions of the ethoxylate heads. As the size of the ethoxylate headgroups becomes greater, the reflectivity profiles decay faster, suggesting that the thickness of the layer mixed with water is increased. The continuous lines are the best fit assuming uniform layer distributions for the headgroups. The good consistency between the calculated curves and the measured ones indicates that to a good approximation



**Figure 7.** Neutron reflectivity profiles for the fully hydrogenated nonyl phenol ethoxylates in  $D_2O$  with n = 4 ( $\oplus$ ), 8 (+), and 12 ( $\triangle$ ). The continuous lines are calculated using uniform layer model and the structural parameters are given in Table 2. The dashed line is the calculated reflectivity from the surface of pure  $D_2O$ .

the distributions of the headgroups are well represented by the uniform layer model.

The increase in the thickness of the water soluble layer may arise from two contributing factors: the broadening of the ethoxylate group layer with n and the increased extent of immersion of the whole surfactant layer into water as a result of the increased affinity of surfactant molecules toward water. The latter has been shown to be unlikely for  $C_{12}E_n$  layers,<sup>26,29</sup> because the distances between the centers of headgroup distributions and those of water were always found to be the same within  $\pm 2$  Å. Hence, the thickness obtained under this water contrast must represent the distributions for the ethoxylate groups. The values were found to be  $16 \pm 2$  Å for BNPE<sub>4</sub>, 18  $\pm$  2 Å for BNPE<sub>8</sub>, and 21  $\pm$  2 Å for BNPE<sub>12</sub>, showing that as the length of the headgroup is tripled, the thickness of the watermiscible layer is only increased by some 30%. The scattering length densities for the layers are all between  $3.1 \times 10^{-6} \text{ Å}^{-2}$ to  $3.6 \times 10^{-6} \text{ Å}^{-2}$ , and are close to the half value of  $\rho$  for bulk  $D_2O$ . The immersed layers are hence well highlighted by the underlying D<sub>2</sub>O subphase. The actual number of water molecules associated with each headgroup can be obtained from the values of  $\rho$ . Each ethoxylate group was found to have two hydrated water molecules, an observation entirely consistent with previous results for  $C_{12}E_n$  series.<sup>17</sup> The physical significance of this value can be assessed by checking the volume constraint within the immersed layer. For example, the volume of  $E_4$  in BNPE<sub>4</sub> is about 250  $Å^3$  and that for eight water molecules is 240  $Å^3$ , making a total of 490 Å<sup>3</sup>, as compared with the value of 575 Å<sup>3</sup> (12.5 Å  $\times$  46 Å<sup>2</sup>) for the total space available. The difference is likely to be caused by the mixing of the hydrophobic fragments into the headgroup as will be discussed later. A similar trend was observed for BNPE8 and BNPE12. It should be noted that such treatment is only approximate as the model itself is very coarse.

The single uniform layer model also fits the reflectivity profiles of chain deuterated surfactants in  $D_2O$ , as shown in Figure 8. This is because the association of  $D_2O$  with the hydrogenated headgroups makes the scattering length density of the headgroup region comparable to that of the deuterated



**Figure 8.** Neutron reflectivity profiles for the nonyl chain deuterated phenol ethoxylates in  $D_2O$  with n = 4 ( $\bullet$ ), 8 (+), and 12 ( $\triangle$ ). The continuous lines are calculated using uniform layer model and the structural parameters are given in Table 2. The dashed line is the calculated reflectivity from the surface of pure  $D_2O$ .

chains. As both the hydrophobic and the hydrophilic groups contribute to the reflectivity, the thickness of the layer offers a good measure of the dimension for the whole layer. Indeed, we have found that in the case of  $C_{12}E_n$  the thickness obtained from the chain deuterated surfactant in D<sub>2</sub>O is within 3 Å identical to that of the fully deuterated surfactant in NRW.15,16 Figure 8 shows a similar trend of depression of reflectivity with the size of the headgroups to that observed in Figure 7, except that the extent of depression is more intensified. The sharp interference fringes occur at a smaller  $\kappa$  close to 0.1 Å <sup>-1</sup>, consistent with the whole layers being thicker than the regions immersed in water. The continuous lines shown in Figure 8 represent the uniform layer fitting and the thickness of the layers was found to be  $23 \pm 3$  Å for BNPE<sub>4</sub>,  $25.5 \pm 3$  Å for BNPE<sub>8</sub>, and  $28 \pm 3$  Å for BNPE<sub>12</sub>. These values together with those obtained from the other two contrasts provide a brief account of the dimensions of the whole layer and the hydrophobic and hydrophilic regions across the interface.

We have previously shown that neutron reflectivity profiles can be alternatively analyzed using kinematic approximation.<sup>26</sup> In the kinematic approach the reflectivity profiles are usually converted into the structural factors,  $h_{ii}$  and  $h_{ij}$ , from which structural parameters are derived more directly. For a surfactant layer adsorbed on the surface of water, the scattering length density profile can be written as

$$\rho(\kappa) = b_{a}n_{a}(z) + b_{w}n_{w}(z) \tag{5}$$

where *a* and *w* refer to surfactant and water. The reflectivity can be approximately expressed  $as^{25,26}$ 

$$R(\kappa) = \frac{16\pi^2}{\kappa^2} \left[ b_a^2 h_{aa}(\kappa) + b_w^2 h_{ww}(\kappa) + 2b_a b_w h_{aw}(\kappa) \right]$$
(6)

where  $h_{aa}(\kappa)$  and  $h_{ww}(\kappa)$  are the partial structure factors describing the distribution of the surfactant and that of the water, respectively, and  $h_{aw}(\kappa)$  is the partial structure factor describing the relative location between the surfactant layer and water distribution across the interface. For alkyl chain deuterated



**Figure 9.** Plots of  $\ln[h_{cc}']$  vs  $\kappa^2$  for the alkyl chain deuterated nonyl phenol ethoxylates in NRW with n = 4 ( $\bullet$ ), 8 (+), and 12 ( $\triangle$ ). The continuous lines are calculated using eq 8 and the structural parameters are given in Table 2.

surfactant in NRW,  $b_w = 0$  and eq 6 becomes

$$h_{\rm cc}' = \frac{R(\kappa)\kappa^2}{16\pi^2 b_c'}$$
(7)

where c denotes the hydrophobic chain and "" indicates that there is a contribution of scattering length from the hydrogenated ethoxylate group to the hydrophobic chain. Although the number density distribution can be obtained from  $h_{cc}$  through Fourier transformation it is usually more convenient to use analytical expressions. For example, if a Gaussian distribution is used to represent surfactant distribution the following relationship exists between  $h_{cc}$  and  $\kappa^{26}$ 

$$\ln h_{cc}'(\kappa) = 2\ln \Gamma - \sigma_c^2 \kappa^2 / 8 \tag{8}$$

where  $\sigma_c$  is the full width at the height of  $n^{\circ}_{c}/e$  ( $n^{\circ}_{c}$  is the maximum number density). Thus the surface excess is obtained from the intercept of the straight line plot of  $\ln h_{cc}'(\kappa)$  versus  $\kappa^2$  and the thickness of the layer from the slope. Figure 9 shows the plots of  $\ln[h_{cc}'(\kappa)]$  versus  $\kappa^2$  for the three surfactants at the cmc. The straight lines through each set of the measured data were calculated using eq 8. The intercept gives  $\Gamma$ , which is within the experimental error consistent with the values obtained from the optical matrix method, as described previously.  $\sigma_{\rm c}$ was found to be  $20 \pm 3$  Å for BNPE<sub>4</sub>,  $22 \pm 3$  Å for BNPE<sub>8</sub>, and 25  $\pm$  3 Å for BNPE<sub>12</sub>. These values are on average about 90% of the corresponding values obtained from the uniform layer model, and the difference is entirely due to the definition of the two models.<sup>26</sup> The good fit of eq 8 to the experimental data shown in Figure 9 shows that the Gaussian distribution is equally good for describing the distribution of the hydrophobic region. Although the measured reflectivity data do not allow a clear distinction to be made between the two models, Gaussian distribution is more realistic because of the effect of roughness and the structural disorder within the surfactant layer, as will be further discussed later. Although model fitting is also used in the kinematic approach, fitting to the partial structure factors is more direct than to the reflectivity profiles because each partial structure factor only contains information about the distribution for a given component at the interface. Uncertainty caused by coupling between different structural parameters is greatly reduced.

The layer fitting based on the optical matrix method does not offer any information about the relative locations between any given pair of components across the interface. Such information can be obtained directly from kinematic approach. Equation 6 can be modified so that the combined reflectivity measurements under the three different isotopic contrasts can be used to determine the cross term in the partial structure factors between the center of the hydrophobic chain and that of water and the new equation is given as follows

$$R(\kappa) = \frac{16\pi^2}{\kappa^2} [b_{\rm c}'^2 h_{\rm cc}'(\kappa) + b_{\rm w}^2 h_{\rm ww}(\kappa) + 2b_{\rm c} b_{\rm w} h_{\rm cw}'(\kappa)]$$
(9)

where "" again indicates the contribution from the hydrophilic headgroup. The cross distance between the center of the hydrophobic region to that of water,  $\delta_{cw}$ , is obtained from the following equation<sup>26,30</sup>

$$h_{\rm cw}'(\kappa) = -\sqrt{h_{\rm cc}'(\kappa)h_{\rm ww}(\kappa)}\sin(\kappa\delta_{\rm cw})$$
(10)

The assumption relating to eq 10 is that the distribution of the hydrophobic region is symmetrical and is close to an even function and that the solvent resembles an odd function. The validity of the assumption has already been previously assessed<sup>30</sup> and for surfactant monolayers the accuracy of  $\delta_{cw}$  is usually very high. The values of  $\delta_{cw}$  were found to be 11.5 ± 1 Å for BNPE<sub>4</sub>, 12.5 ± 1 Å for BNPE<sub>8</sub>, and 13 ± 1 Å for BNPE<sub>12</sub>.

The presence of surfactant at the surface of water also affects the water distribution at the interface. The decay of water density can be represented by a tanh function<sup>26</sup> and  $h_{ww}(\kappa)$  can be written as

$$h_{\rm ww}(\kappa) = n_{\rm wo}^{2} (\pi \kappa \delta_{cw} \xi/2)^2 {\rm csch}^2(\pi \xi \kappa/2)$$
(11)

where  $\xi$  is the width parameter of the tanh function and  $n_{wo}$  is the number density of bulk water. For a pure water surface,  $\xi$ is about 2 Å. The penetration of the surfactant headgroups disrupts the distribution of water, resulting in a broader width of water density profile; and accordingly,  $\xi$  is much greater. The values of  $\xi$  were found to be  $8 \pm 1$  Å for BNPE<sub>4</sub>,  $10 \pm 1$ Å for BNPE<sub>8</sub>, and  $13 \pm 1$  Å for BNPE<sub>12</sub>, showing that the adsorption of surfactant has significantly disturbed water distribution.

The analysis described above offers no direct information about the distribution of the ethoxylate head and how it mixes with water. We have previously shown that useful information relating to the headgroup distribution can be extracted with measurable reliability from the simultaneous least-squares fitting to the three reflectivity profiles using the analytical expressions to represent the distributions of the three components and the relations between them. In this analysis, the distributions of the hydrophobic chains and the ethoxylate headgroups are represented by the Gaussian function and that of water by tanh function. The relations between them can be described by eq 10 except for the relative location between the hydrophobic chain and the hydrophilic headgroup. The term of  $\sin(\kappa \delta_{cw})$ should be replaced by  $\cos(\kappa \delta_{cw})$  because both distributions are now even functions.<sup>26</sup> The combined equations lead to five unknown parameters: the thicknesses of the nonyl phenol layer and the ethoxylate head, the width parameter for water distribution, and the distances between the hydrophobic layer and water, and between the head layer and water. Table 3 lists the

TABLE 3: Structural Parameters for  $BNPE_m$  and  $C_{12}E_m$  at Their cmcs

parameters	$BNPE_4/C_{12}E_4$	$BNPE_8/C_{12}E_8$	$BNPE_{12}/C_{12}E_{12}$
$A/Å^2$	$46 \pm 3/44 \pm 3$	$61 \pm 3/62 \pm 3$	$72\pm5/75\pm5$
$\sigma_{ m c}\pm 2/{ m \AA}$	18/16.5	19/15	22/15
$\sigma_{ m h}\pm4/ m \AA$	14/14	18/19	22/21.5
$\delta_{ m cw}\pm 1/{ m \AA}$	11/9.5	13/11	14/13
$\delta_{ m hw}\pm 1/ m \AA$	0.3/2	1/0.5	1/1
$\xi \pm 1/\text{\AA}$	8/7.5	10/9	13/12

parameters obtained and the values of  $\delta_{\rm cw}$ ,  $\xi$ , and  $\sigma_{\rm c}$  are consistent with those obtained from the direct analysis based on eq 9. The values of  $\delta_{hw}$  are always around  $1 \pm 1$  Å, showing that the centers of the headgroup distributions are almost at the same positions as those for the water. The sensitivity of the fitting to the structural parameters was tested by varying a given parameter while fixing the others at their optimal values. It was found that the reflectivities were sensitive to the variation in  $\delta_{\rm cw}, \delta_{\rm hw}, \xi$ , and  $\sigma_{\rm c}$ , but insensitive to  $\sigma_{\rm h}$ . The errors quoted in Table 3 reflect the range of variation over which no obvious difference between the measured reflectivities and the fitted ones was observed. It should be pointed out that such a treatment can only provide some approximate estimate of the distributions of the headgroup and its location relative to other components. More reliable information on  $\sigma_h$  and  $\delta_{hw}$  can only be obtained by measuring the reflectivity profiles using the head deuterated samples.

The distributions of different fragments in terms of volume fractions along the surface normal are plotted in Figure 10 for all three surfactants. Gaussian distributions have been used for the hydrophobic chain and the head, and tanh function for the distribution of water. The extent of mixing between different fragments can be seen from the overlapped areas in Figure 10. The distribution of the total volume fraction is also plotted for each surfactant and the variation is within  $\pm 10\%$  when approaching the bulk density, showing a good self-consistency between the data. We have previously discussed that the main errors arise from the insensitivity of the reflectivities to the shape of the distributions, e.g., Gaussian distributions for the hydrophobic chain and hydrophilic head, and tanh function for water.<sup>26</sup> Although the trend of water distribution resembles a tanh function, the exact shape may not follow a tanh profile precisely. The deviation is usually the main source of error contributing to the variation in the total volume fraction distribution.

The fully extended length of the branched nonyl phenol group is about 10 Å. The thicknesses for the nonyl phenol layers obtained are around 20 Å, showing that the hydrophobic groups are twice as thick as their fully extended length. As the size of the headgroups increases the width of the hydrophobic layers also increases, clearly showing that as n increases the distributions of the hydrophobic chains are further broadened. The thicknesses measured on the surface of water contain contributions arising from capillary wave roughness and structural disorder. The relationship between the intrinsic thickness of the surfactant monolayer in the direction normal to the surface  $(l_z)$ and the roughness ( $\omega$ ) can be approximately expressed by<sup>29</sup>

$$\sigma^2 = l_z^2 + \omega^2 \tag{12}$$

The value of  $l_z$  depends on contributions from the extended component lengths, different chain conformations, and the average distribution of orientations with respect to the surface normal. There are two types of roughness: structural disorder within the layer and thermal roughness arising from capillary waves. The contribution of thermal roughness can be estimated using the relationship developed by Schwartz et al.<sup>31</sup> for the surface of pure liquid. Schwartz et al.<sup>31</sup> have shown that the



**Figure 10.** Volume fraction distributions for  $BNPE_4$  (a),  $BNPE_8$  (b), and  $BNPE_{12}$  (c) at their cmcs. The continuous lines denote the alkyl chain; the long dashed lines denote the headgroups; the short dashed lines denote the water and the long and short dashed lines denote the total volume fraction distributions. The reference points are at the centers of the hydrophobic chain distributions.

capillary wave amplitude of a pure liquid varies inversely as the square root of surface tension. For example, the surface tension of BNPE<sub>4</sub> at its cmc is 29 mN m<sup>-1</sup>, and this will give a capillary wave roughness of about 4.4 Å. Since unit mean square amplitude in terms of capillary waves is equivalent to 2.3 units in terms of the distributions used in the present work, the thermal roughness of 4.4 Å at the cmc is then equivalent to 10 Å in our analysis and will contribute to the broadening of the whole monolayer in the form as described in eq  $12.^{31}$  As the thickness for the hydrophobic chain is 18 Å, removal of 10 Å according to eq 12 leads to a length of 14.5 Å projected onto the surface normal. This thickness is still much greater than the value of about 10 Å for the fully extended length of the branched hydrophobic chain. The result hence implies considerable structural roughness within the surfactant layer.

The effect of alkyl chain length on the thickness of the adsorbed surfactant layers has been examined in our previous studies on the adsorption of the cationic series  $C_m$  TAB on the surface of water.<sup>32</sup> It was found that when m = 12 the thickness of the alkyl chain layer is effectively the same as the fully extended length. As the chain length is increased, the alkyl chain layers become thinner than the fully extended lengths. For example, the thickness of the alkyl chain layer formed by C18 TAB at its cmc is about  $16.5 \pm 1$  Å and the fully extended length is 24.3 Å, showing that the layer is dense and is effectively tilted. However, in the case of C<sub>8</sub> TAB whose fully extended alkyl chain length is 10.5 Å, the alkyl chain layer was found to be 15.5 Å, suggesting an increased level of structural disorder within the adsorbed layer. In a separate study of the adsorption of short chain alcohols on the surface of water we also found that for both ethanol and butanol the adsorbed layers are thicker than the fully extended lengths of the alcohol molecules.<sup>32</sup> For the nonionic surfactant series, we have only studied the  $C_{12}E_n$  series. Hence the possible effect of the length of the alkyl chains on the distributions of the fragments in the layers is not well established. Nevertheless, for all the  $C_{12}E_n$ species studied, the thickness of the dodecyl chain layer is always less than its fully extended length. This is especially so when the size of the ethoxylate group is large. In comparison with these results it appears that the behavior of the branched nonyl phenol ethoxylates resembles those with short alkyl chains. It is not clear at this stage how the inclusion of the benzyl ring affects the distribution of different fragments within the adsorbed layer, but what is clear is that the insertion of the benzyl ring has dramatically reduced the cmc for this series of surfactants.

It is useful to compare  $BNPE_n$  distributions with those of  $C_{12}E_n$  layers at the same n. The comparison is given in Table 3. It can be seen that although there are differences between cross distances between the centers of distributions, the differences are mostly within 2 Å. For both series of surfactants, the extent of mixing increases with the size of the headgroups. All the width parameters are comparable except the thickness of the hydrophobic layers. The thicker hydrophobic chain region within BNPE<sub>n</sub> layers clearly indicates a stronger mixing between the hydrophobic chains and the hydrophilic headgroups, and between the hydrophobic chains and water. The increased mixing may arise from the presence of phenol groups that offer high affinity to the ethoxylate headgroups, but it should be remembered that in comparison with the straight dodecyl chains, the nonyl phenol groups differ in the length of alkyl chain, the branching and the insertion of benzyl ring. Further work is required to disentangle the effects of these structural differences on the extent of mixing within the adsorbed layers.

#### Conclusions

Changes in the chemical configuration of the hydrophobic chain affects the adsorption and aggregation properties of nonionic surfactants. Although the rate of decrease of the cmc with the increase of carbon number in the hydrophobic chains is the same for  $C_mE_n$  and APE surfactants, the cmc of APEs increases 3 times faster with the length of the ethoxylate units. The change in the structure of the hydrophobic chain affects

the distribution of the hydropbobic layer, but does not alter the limiting area per molecule at the cmc. The much thicker hydrophobic layer caused by the branching of the alkyl chain and the insertion of the benzyl ring underlines a large extent of mixing between the hydrophobic groups and the ethoxylate headgroups, and is indicative of a high affinity of the hydrophobic alkyl phenols toward the hydrophilic ethoxylate headgroups.

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