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The partition of ethoxylated non-ionic surfactants between two non-miscible phases

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Abstract The partition of a polydispersed ethoxylated non-ionic surfactant in equilibrated oil–water systems has been studied at 25 °C. The model surfactant used was a commercial sample of nonylphenol ethoxylated with 10 moles of ethylene oxide ($NPEO_{10}$). The partition isotherms over the range of surfactant concentration including the critical micelle concentration (CMC) were made with *n*-hexane, *i*-octane and *n*-decane as oil phases. Each partition isotherm exhibits a change of slope that matched the CMC value of surfactant determined by surface tension measurements on aqueous solutions. During the partition of $NPEO_{10}$ in the oil–water systems, the oligomer distribution in the oil and water phases changed because of fractionation. Below CMC, the mean ethoxylation degree in the oil phase was smaller, whereas in water it was higher than the mean initial value of the surfactant. Moreover, the mean ethoxylation degree in both oil and water phase was practically independent of surfactant concentration. Above CMC, the mean distribution of ethoxymers decreased in both phases. This was ascribed to the competition between micelles from water and the oil phase for the more hydrophobic species of the surfactant. The mean distribution of ethoxymers in the aqueous phase asymptoted to a value that was the mean of the surfactant itself, whereas it steeply decreased in the organic phase.

Keywords Non-ionic surfactants · Polyethoxylated nonylphenols · Ethoxymer distribution · Partition isotherms · Critical micelle concentration (CMC)

Introduction

Ethoxylated non-ionic surfactants are widely used in various industrial and household applications as detergents, emulsifiers, wetting agents, cosmetic additives, enhanced oil recovery agents, etc. Their properties and uses largely depend on the balance between the hydrophilic propensity of their polar poly(ethylene oxide) (PEO) chain and the lipophilic tendency of the hydrocarbon tail. To quantify this balance the hydrophile-lipophile balance (HLB), the solubility parameter (δ_0), and the oil–water partition coefficient (K_{ow}) are used [1]. The partition coefficient of a compound often parallels its biological effects. Consideration of this parameter in structure-toxicity or structure-activity studies might substantially contribute to the assessment of the ecological impact of surfactants. At the same time, the knowledge of partition behavior is useful for application purposes. For instance, in emulsification it controls not only whether the emulsion will be of the water-in-oil (W/O) or oil-in-water (O/W) type, but also its stability and phase inversion [2, 3]. As most of the accessible non-ionic surfactants are polyethoxylated products with a wide distribution of the ethylene oxide chain length, in some circumstances each of the molecular species could manifest individual tendencies. For example, the use of polydisperse ethoxylated surfactants in oil–water systems may lead to different partition of the species between the system phases, and the phase behavior is peculiarly affected by surfactant concentration, ratio of phases, temperature, electrolytes etc. [4–6]. Therefore, the understanding of phase behavior is difficult and cannot be achieved without detailed study of surfactant partition between two non-miscible phases.

This work aims to investigate the partition behavior of an ethoxylated nonylphenol with 10 EO units ($NPEO_{10}$) in oil–water systems. The critical micelle concentration (CMC) values obtained with the aid of partition isotherms are compared with those from the surface tension measurements. The paper also points toward analyzing the change of the $NPEO_{10}$ oligomer distribution in the oil and aqueous phase as a result of fractionation between them. The experimental results obtained in this study are in agreement with the theoretical model for the partition of polydisperse ethoxylated surfactants between two non-miscible phases.

Experimental

Materials

The commercial product Lutensol AP-10 (i.e., nonylphenol ethoxylated with 10 moles of ethylene oxide, $NPEO_{10}$) was purchased from BASF A. G., Ludwigshafen, Germany. The homogeneous ethoxylated nonylphenols namely, triethylene glycol monononylphenyl ether (NPE_3) and octaethylene glycol monononylphenyl ether (NPE_8), used to identify the ethoxymers, were prepared as previously described [7]. HPLC and spectroscopic grade reagents were used for chromatographic and partition experiments. Double distilled water having an electrical conductivity lower than 1.5 μS/cm was employed.

Apparatus

The chromatographic measurements were carried out with a high-performance liquid chromatograph Hewlett-Packard (Boeblingen-Germany) model 1084B, fitted with a variable wavelength UV detector 79 875A, set at 280 nm. Analytical column (200×4.6 mm I. D.) packed with irregular silica (Si-100, 5 μm), was purchased from Hewlett-Packard (Waldbronn, Germany). The flow rate was of 1 ml/min. The column temperature was of 25 °C. The UV absorbance was measured on a SPECORD M40 (Carl Zeiss, Jena, Germany) spectrophotometer. Surface tension measurements were done with the aid of du Noüy ring method at 25 °C.

Methods

The critical micelle concentration of the polydisperse ethoxylated nonylphenol ($NPEO_{10}$) sample was determined by the surface tension method based on the fact that above the CMC the surface activity is almost constant and increases sharply below it. The surface tension values were plotted against the logarithm of surfactant concentration and the CMC was found at the intercept point of the two linear parts of the graph [8].

The partition isotherms of $NPEO_{10}$ in the oil–water systems were carried out by contacting the equal volumes of aqueous and oil phases in tightly closed vials. The oil–water volume ratio was kept constant at one for all systems. Aqueous solutions of $NPEO_{10}$ having concentrations within the 10^{-5}–10^{-3} M range were prepared. The samples were maintained at 25 ± 0.5 °C for 3 months to attain the equilibrium. The surfactant concentration in the equilibrated water phases was determined from the absorbance at 280 nm, and that in the oil phases was obtained by difference.

To determine the ethoxymer distribution of the $NPEO_{10}$ as a result of partition, the equilibrated phases were separated and the solvents evaporated off. The residues were analyzed by normal-phase high-performance liquid chromatography (NP-HPLC) following the same procedure as described in [9]. The mean ethoxylation degree was calculated in a similar way to that given elsewhere [10].

Results and discussion

Partition isotherms

Figure 1 illustrates the partition isotherm of $NPEO_{10}$ in the *n*-hexane–water system. Similar isotherms were obtained for this surfactant in *i*-octane–water and *n*-decane–water. They reveal that when the total amount of surfactant increases, the change of surfactant concentration in oil versus that in water has a well-defined break-point delineating two distinct regions. In the lower concentration region (Fig. 1a) the slope is higher than in the higher concentration region (Fig. 1b), and denotes that above the break-point a greater amount of surfactant goes into aqueous than in organic phase. This kind of isotherm is typical for polydispersed ethoxylated surfactants [2, 11–14]. To explain this behavior one may consider the simpler case of partitioning the homogeneously ethoxylated surfactants. For example, a previous partition study on the cyclohexane–water systems revealed that above the break-point the surfactant concentration was constant in water for NPE_6, whereas for NPE_8 it did not change in oil [15]. The break-point appearing in the partition isotherm was assigned to the beginning of surfactant aggregation, namely to the

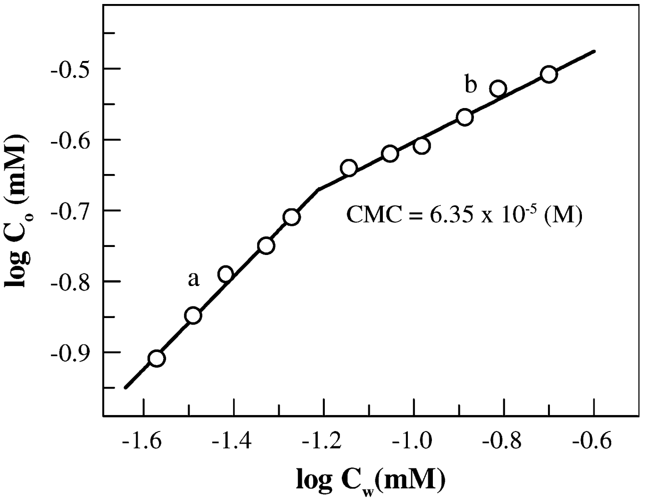

Fig. 1 Partition isotherm of $NPEO_{10}$ in the *n*-hexane–water system at 25 °C. **a** Premicellar zone. **b** Micellar zone

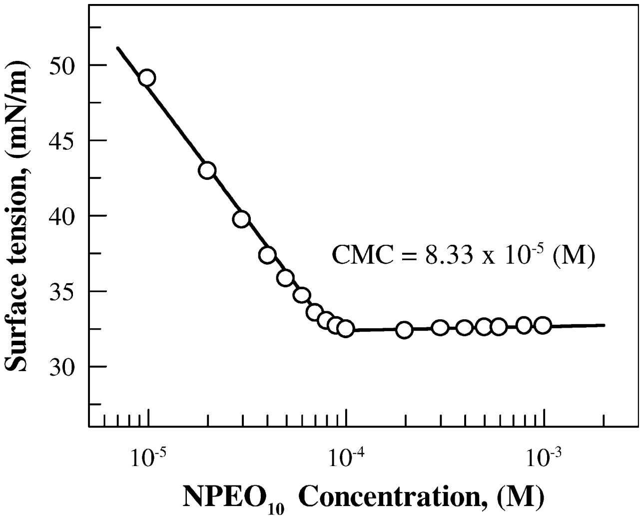

Fig. 2 Surface tension isotherm of $NPEO_{10}$ in water at 25 °C

CMC. It meant that for the hydrophobic NPE_6 surfactant the aggregates did form in the oil phase and for the hydrophilic NPE_8, in water. However, when the system contained the NPE_6-NPE_8 (1:1, w/w) mixture, the surfactant concentration gradually increased in the oil phase above CMC. Therefore, the system containing the simplest binary surfactant mixture did deviate from the partition of a single surfactant and behaved in a manner similar to that observed by us for $NPEO_{10}$ and previously reported by other authors for normally distributed ethoxylated surfactants [2, 11–14]. The allure of the curve in Fig. 1 is explained taking into account that above CMC more surfactant is distributed in water than in oil, and supports the idea that micelles are formed in the aqueous phase.

Data in the literature, concerning the occurrence of CMC in the oil phase are very scarce as compared with those concerning its occurrence in water. The behavior of non-ionic surfactants still remains a topic of debate, with some scientists suggesting that a gradual aggregation occurs over a very wide range of surfactant concentrations [16, 17]. It was noticed that in organic solvents the aggregation numbers of ethoxylated surfactants are lower (i.e., 4–12) than those in aqueous solutions (~100). They increased with the length of the EO chains, but the alkyl chain of surfactants has no influence. The length of the hydrocarbon chain of the solvent molecules and the presence of water favored the aggregation process. The ^{1}H RMN measurements showed that aggregate formation in hexane of polydisperse ethoxylated nonylphenols could be neglected [13]. Consequently, one could infer that in our hexane–water system, the break-point in the partition isotherm corresponds to the equilibrium concentration of the surfactant at which the micelles appear in the aqueous phase.

The change of slope in Fig. 1 occurs at a surfactant concentration in water equal to 6.35×10^{-5} M, which can be considered as being the CMC of the $NPEO_{10}$ in that phase. The values corresponding to the break-point in the isotherms for *i*-octane–water and *n*-decane–water systems were of 10.02 and 11.80×10^{-5} M, respectively. They correspond to total surfactant concentrations in the oil–water systems of 27.90×10^{-5} M (*n*-hexane–water), 32.15×10^{-5} M (*i*-octane–water) and 30.55×10^{-5} M (*n*-decane–water). The CMC values obtained from the partition isotherms are comparable with that of 8.33×10^{-5} M determined from the surface tension isotherm of $NPEO_{10}$ (see Fig. 2). One may notice that the CMC values derived from the partition isotherms increase in the following order: *n*-hexane < *i*-octane < *n*-decane. At the same time, the CMC in *n*-hexane–water is smaller, whereas those for *i*-octane–water and *n*-decane–water systems are higher than the values determined by surface tension. To explain these results, one has to take into account preferential extraction in oil of the hydrophobic ethoxylates. It produces an increase of the mean ethoxylation degree of the surfactant in water and increases the CMC. In contrast, addition of hydrocarbons to aqueous surfactant solutions reduces the CMC, the effect being more evident as the hydrocarbons are more polar [18, 19]. These two opposite tendencies account for the CMC values recorded in our systems.

We generalized the treatment proposed by Clint [20] to calculate the CMC for the binary surfactant mixture and computed the critical micelle concentration of $NPEO_{10}$. In doing so, we used the NP-HPLC results revealing that $NPEO_{10}$ contains oligomers having from 2 to 19 EO groups in the molecule [9], and the CMC values graphically estimated from the data of homogeneously ethoxylated nonylphenols [21]. The CMC found was of 5.74×10^{-5} M being comparable with the values obtained from surface tension and partition measurements.

The continuous increase of surfactant concentration in the oil phase observed in the partition isotherms of $NPEO_{10}$ beyond CMC, could be related to the presence in system of the mixture of ethoxymers having their molecules with the same hydrophobic part but different PEO chain length and hence, dissimilar hydrophilic–lipophilic properties. This will result in a variation of their oil–water partition coefficients [2, 3]. One found that for homogeneous ethoxylated nonylphenols with less than 10 EO groups in molecule, the K_{ow} is supraunitary; whereas, it is subunitary above this EO number [22]. It means that for the surfactants with ethoxylation degree smaller than 10, the solubility is higher in oil than in water. Linear relationships were established between the K_{ow} values of homogeneous ethoxylated nonylphenols and their EO unit number [22] which allowed us to calculate the standard free energy change corresponding to the transfer of one EO group from oil to water. It was of −2.30 kJ/mol (−550 cal/mol) and of −1.71 kJ/mol (−409 cal/mol) for ethoxylated nonylphenols in *i*-octane–water, and in *n*-decane–water, respectively. The values were very close to those of −2.51 kJ/mol (−600 cal/mol) reported for homogeneously ethoxylated octylphenols [1, 23] and of −2.61 kJ/mol (624 cal/mol) for homogeneous poly(oxyethylene glycol *n*-dodecylethers) [24] in *i*-octane–water systems. The negative sign of the standard free energy indicates that the transfer of hydrophilic EO group from oil to water occurs spontaneously.

Ethoxymer distribution during partition

To shed light on the partition behavior of $NPEO_{10}$ observed in Fig. 1, the oligomer distribution, resulting after partition in the aqueous and organic phases, was determined by NP-HPLC. One has to recall that the analysis of the $NPEO_{10}$ surfactant before the partition showed that the sample contained from 2 to 19 detectable ethoxymers and the computed mean EO number was 9.45.

Figure 3 illustrates the change of the mean ethoxymer distribution of $NPEO_{10}$ with the overall surfactant concentration in the *n*-hexane–water system. Similar results were recorded for the partition of $NPEO_{10}$ in *i*-octane–water and *n*-decane–water systems. They show that the mean ethoxylation degree is different in oil from that in water. For example, at a total surfactant concentration of 10^{-4} M, the mean ethoxylation degree of the species in the *n*-hexane phase was 7.10. Ethoxymers with longer EO chains were detected in water and they had a mean ethoxylation degree of 10.65. At low surfactant levels in the premicellar range, the ethoxymer distribution indicated the preferential fractionation of the more hydrophobic oligomers in oil, whereas those more hydrophilic were concentrated in water, but the mean EO number remained constant in both phases. With further increase of the total surfactant concentration in the system, there was a point where the ethoxymer distribution did change in both phases. This point corresponds to the equilibrium concentration of the surfactant at which CMC is reached. However, one should expect that in Fig. 3 the change in the mean EO number in the aqueous phase would correspond with that in the oil. The observed discrepancy was ascribed to experimental errors, since the difference in the total surfactant concentrations (i.e., 2×10^{-4} and 2.5×10^{-4} M) at which the ethoxymer distribution in oil and in water, respectively, begins decreasing is very small. These values are comparable with the total surfactant concentration in the system corresponding to the break-point in the partition isotherm (i.e., 2.79×10^{-4} M).

Above CMC, the mean ethoxylation degree began to decrease in both phases. At a total surfactant concentration of 4.5×10^{-4} M, the mean EO number determined in oil was 6.80, being smaller than that measured in the premicellar range. It was 9.48 in water, which indicated a mean EO number almost identical to that of $NPEO_{10}$ before partition. The explanation of these results is that as the overall surfactant concentration increases, the micellar pseudo-phase in water gets enriched in hydrophobic components and the composition comes close to that of the initial surfactant [12, 13, 25]. The decrease of oligomer mean EO number in oil above CMC proves the existence of a competition between oil and the micelles

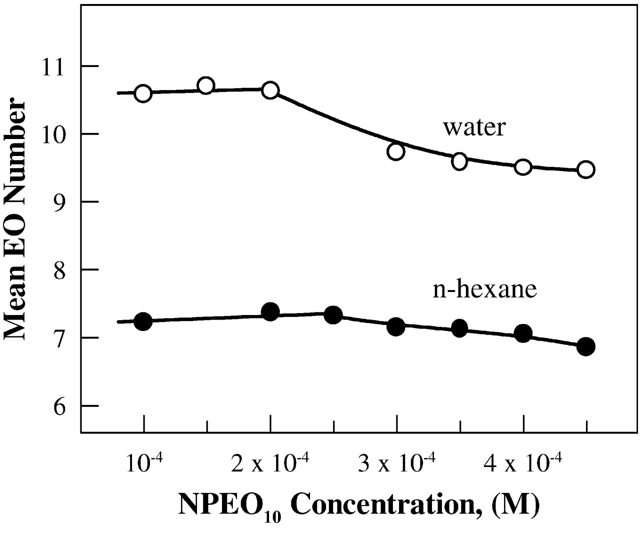

Fig. 3 The mean EO number of oligomers partitioned at equilibrium in water and *n*-hexane as a function of total $NPEO_{10}$ concentration

from water for the hydrophobic ethoxymers, as previously suggested [12, 13, 25].

The selective partition of ethoxymers between oil and water determines the phase inversion temperature (PIT) behavior observed for emulsions stabilized with polydisperse non-ionic surfactants. In this case, PIT increases with the lowering of the surfactant concentration, and has a steep rise especially at low concentration, but when a homogeneous non-ionic surfactant is used PIT remained practically constant, regardless of the change of concentration [2, 15]. This was explained by considering the dependence of PIT on the hydrophilic–lipophilic properties of the surfactants. Owing to the preferential fractionation of the part homologous with the shorter EO chain into the oil phase, the surfactants in water have longer hydrated EO chains and consequently, the PIT increases. The decrease of PIT with the total surfactant concentration was attributed to changes in the composition of mixed micelles, namely to their enrichment in more hydrophobic components [2, 12, 25]. Such phenomena do not occur in the case of homogeneously ethoxylated surfactants. Therefore, when the surfactant concentration exceeds the CMC, its mean ethoxylation degree in the aqueous phase will decrease, as observed in Fig. 3.

Our experimental data on the partition of $NPEO_{10}$ in the oil–water systems are in agreement with the theoretical treatment of this process [12, 13, 25]. The model relies on ideal mixing and phase separation for micellization. It predicts that, as the surfactant concentration in the system exceeds CMC, the mixed micelles in water get enriched in the more hydrophobic species of the mixture, and their composition is likely to match that of the initial surfactant. Owing to competition between the micelles and the oil phase for the total surfactant, the hydrophilicity of the mixed surfactant decreases in both phases, which is obviously valid in our case too.

Conclusions

The partition isotherms obtained for $NPEO_{10}$ in various oil–water systems were typical for the polydisperse ethoxylated surfactants. Their break-point was assigned to the CMC and was consistent with the value determined from the surface tension isotherm by using aqueous solutions. The equilibrated oil and water phases had different ethoxymer distribution from that of the initial surfactant. The partition depended on the total surfactant concentration in the system. Below CMC, the mean EO number of the surfactant in water and oil was higher and lower, respectively, than the mean ethoxylation degree of the initial $NPEO_{10}$. Above CMC, the mean EO number in water approached the initial ethoxylation degree of the surfactant, whereas in oil it steadily decreased. The results obtained in this study are consistent with those from previous partition data and with the theoretical partition model of polydisperse ethoxylated surfactants between two non-miscible phases.

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