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INFLUENCE OF SYNERGETIC EFFECTS OF OXYETHYLATED ISONONYLPHENOL AND POLYGLYCERYL-3 METHYLGLUCOSE DISTEARATE ON THE FORMATION OF SELF-ORGANIZING STRUCTURES AT THE WATER / VAZELINE OIL INTERFACE

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In this research, the surfactant – co-surfactant intermolecular interactions in the H2O – Oxyethylated Isononylphenol – Polyglyceryl-3 Methylglucose Distearate – Vaseline oil system were studied. For the first time, two approaches were combined: the additivity of hydrophilic lipophilic balance (HLB) and the water / oil interfacial tension measurement in microemulsion systems. It was shown that by calculating the HLB of the surfactant mixture and measuring the corresponding interfacial tension, it is possible to predict self-organization of surfactant. It was directly related to the intermolecular interaction estimated by calculating the interaction parameter β. It has been established that in mixed systems synergistic effects were observed and the interfacial tension decreased, which were caused by electrostatic attraction between surfactant’s molecules. The processes of self-organization of surfactant mixture at the H2O – Vaseline oil interface were studied. It has been shown that the hydrophilic lipophilic balance of the mixture and the interaction parameter β directly connected with the nature of the structures from liquid crystal to microemulsion. The proposed approach can be used for the scientifically based calculation of the components in the surfactant mixture at the liquid – liquid interface and prediction of microemulsion and liquid crystals formation in three component systems.

Key words: liquid crystals, microemulsions, mixed surfactants, interfacial tension, adsorption, synergism, hydrophilic lipophilic balance, interaction parameter.

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ВЗАИМОСВЯЗЬ СИНЕРГЕТИЧЕСКИХ ЭФФЕКТОВ ОКСИЭТИЛИРОВАННОГО ИЗОНОНИЛФЕНОЛА И ПОЛИГЛИЦЕРИЛ-3 МЕТИЛГЛЮКОЗЫ ДИСТЕАРАТА НА МЕЖФАЗНОЙ ГРАНИЦЕ ВОДА / ВАЗЕЛИНОВОЕ МАСЛО С ХАРАКТЕРОМ ОБРАЗОВАНИЯ САМООРГАНИЗУЮЩИХСЯ СТРУКТУР

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Исследовано межмолекулярное взаимодействие ПАВ/со-ПАВ в системе вода – оксиэтилированный изононилфенол – полиэтиленлициерил-3 метилглюкозы дистеарат – вазелиновое масло. Впервые совмещено два подхода: принят аддитивности гидрофильно-липофильного баланса (ГЛБ) и измерение межфазного натяжения жидкость/жидкость. Показано, что путем расчета ГЛБ смеси ПАВ и измерения соответствующего межфазного натяжения можно прогнозировать самоорганизацию ПАВ, что непосредственно связано с межмолекулярным взаимодействием, оцененным путем расчета параметра взаимодействия на границе раздела и в смешанных мицеллах ПАВ. Установлено, что в смешанных системах наблюдаются синергетические эффекты снижения межфазного натяжения, обусловленные электростатическим притяжением между молекулами ПАВ. Исследованы процессы самоорганизации смеси оксиэтилированного изононилфенола и полиэтиленлициерил-3 метилглюкозы дистеарата на границе раздела вода / вазелиновое масло. Показано, что ГЛБ смеси и параметр взаимодействия непосредственно связаны с характером образования структур от жидкокристаллических до микромульсционных. Таким образом, путем измерения...
formation of liquid crystal and microemulsion structures in the H₂O – Lecithin – Propylene glycol – Vaseline oil system [18, 19]. In the present work, an assumption about the connection of the surfactant mixture’s HLB and interfacial tension, which is influenced on the surfactant – co-surfactant interaction and surfactants self-organization at the water – oil interface, was made.

The aim of this work was to develop a colloidal-chemical approach for calculation of the surfactant’s concentration ratios in the mixture, taking into account the interaction of two surfactant molecules at the water – oil interface applying H₂O – Polyglyceryl-3 Methylglucose Distearate (PMD) – Oxyethylated (OE) Isononylphenol – Vaseline oil system as a model.

Experimental

Commercially available surfactants such as OE Isononylphenol with a degree of oxyethylation n = 8 (laboratory of Nizhnekamskneftekhim) and biodegradable compound Polyglyceryl-3 Methylglucose Distearate (Croda, Germany) were used for the preparation of systems. The non-polar phase was medical Vaseline oil (Sigma Aldrich). In the experiment, bidistilled water with electrical conductivity no more than 0.056 μS / cm was used.

To obtain a multicomponent H₂O – OE Isononylphenol – PMD – Vaseline oil systems, the calculated weight of the surfactant mixture was dissolved in oil heated to 70 °C with slow stirring for 4 hours. Then, the systems were cooled to 40 °C and bidistilled water was added. The resulting mixture was stirred in an YX 2100 ultrasonic homogenizer at a frequency of 50 kHz for 8 h. Before testing, samples kept at room temperature for 7 days to achieve equilibrium.

The obtained lyomesophases were identified using the polarization optical microscopy (POM) on the Olympus BX51 microscope (Olympus Optical Co., Japan) with a video camera and Linkam high-precision temperature-controlled system. Interfacial tension of surfactants and their mixtures at the H₂O – oil interface was measured on the stalagmometer ST-2.
Results and discussion

For construction of phase diagrams of self-organizing multicomponent systems it is often required to select a system of two surfactants. However, the optimal concentration ratios of surfactants – co-surfactants are often found out after the construction of the diagrams, by analyzing the areas of various self-organizing structures, which is quite laborious. For example, the authors of [20] constructed the Water – Tween 80 – Transcutol P-oleic acid phase diagrams. In this case, the ratio Tween 80 – Transcutol P was 1:0, 1:1, 1:2, 2:1, 1:3, 3:1, 1:4, 4:1. Optimal surfactants ratio of 2:1 was selected; as a result an extensive microemulsion region is formed. The surfactant ratios were chosen without taking into account the HLB values.

As surfactants have specific HLB, in the presence of a limited number of them, binary mixtures of these surfactants can be obtained, based on the principle of additivity of HLB. Mass fraction of surfactant (\(W_1\) and \(W_2\)) is determined by solving the system of equations:

\[
\begin{align*}
W_1 \cdot HLB_1 + W_2 \cdot HLB_2 &= HLB \\
W_1 + W_2 &= 1
\end{align*}
\]

where HLB, HLB and HLB are the hydrophilic lipophilic balances of the first, second surfactant and their mixture [21]. According to this equation system, the mass fractions of OE Isononylphenol and PMD in the mixture were calculated (Table 1).

| № mixture | HLB of the mixed surfactant | \(W_1\), % | \(W_2\), % |
|-----------|---------------------------|------------|------------|
| 1         | 5.6                      | 100        | 0          |
| 2         | 6                        | 94         | 6          |
| 3         | 7                        | 78         | 22         |
| 4         | 8                        | 62         | 38         |
| 5         | 9                        | 47         | 53         |
| 6         | 10                       | 31         | 69         |
| 7         | 11                       | 16         | 84         |
| 8         | 12                       | 0          | 100        |

The obtaining of ME systems is possible only at the critical interfacial tension values close to zero, whereas this condition is not necessary for the synthesis of mesomorphic compounds. In this regard, the interfacial tension of surfactant mixtures at the water – Vaseline oil interface was measured at various weight ratios according to the principle of additivity of HLB (equation 1) [21] (Fig. 1).

With an increase in the PMD content, the interfacial tension increases. This can be explained by the fact that PMD more often forms liquid crystal structures, and low interfacial tension is observed for surfactants that are stabilizers of ME.

The lowest value of \(\gamma\) was observed at HLB of the mixture № 6. Therefore, it can be assumed that the corresponding ratio of surfactant : co-surfactant provides maximum surfactant activity and the formation of stable ME systems.

Based on the data of tensiometric studies, the main adsorption characteristics of the systems at the water – Vaseline oil interface were calculated, such as maximum adsorption, the area per molecule and the thickness of the adsorption layer (Table 2). The values of CMC are obtained graphically from interfacial tension isotherms.
Table 2. Adsorption characteristics of systems at the water / Vaseline oil interface

| System                                      | $A_\infty \cdot 10^6$, mol/m² | $S_0 \cdot 10^{20}$, m² | $\delta$, nm | CMC, mM |
|---------------------------------------------|-------------------------------|--------------------------|--------------|--------|
| H₂O – OE Isononylphenol – Vaseline oil     | 15,95                         | 10,4                     | 9,1          | 0,17   |
| H₂O – PMD – Vaseline Oil                   | 11,4                          | 14,57                    | 75,2         | 0,12   |
| H₂O – OE Isononylphenol – PMD – Vaseline Oil | 18,25                        | 9,1                      | 17           | 0,1    |

From the data in the Table 2 follows that adding co-surfactant increases the adsorption capacity ($A_\infty$) and decrease the CMC to lower values, which occurs due to a change in conformation of molecules, an increase in the size of the hydrocarbon fragment ($\delta$) and a decrease in the polar portion of the surfactant molecule ($S_0$). This is probably due to the fact that when co-surfactants are added, Isononylphenol molecules are reoriented due to the incorporation of PMD molecules between their molecules and the hydrocarbon tails take a more vertical position on the water / oil interface, thereby stabilizing the system (Fig. 2).

According to it, the nature and strength of the interaction between two surface active substances can be determined by calculating the interaction parameters $\beta^\sigma$ in mixed adsorption layers, which are found using graphs of interfacial tension ($\gamma$) versus concentration (C) of aqueous solutions of individual surfactants and their mixtures. The lower the $\beta^\sigma$ value, the stronger the interaction between surfactants.

A difference was made between the surfactant interaction parameter at the water – oil interface $\beta^\sigma$ and the interaction parameter in mixed micelles in the solution volume $\beta^m$.

The interaction parameter for the mixed formation of a surfactant monolayer at the water – oil interface can be calculated by the formulas:

$$\begin{align*}
(X_i^\alpha)^2 \ln \left( \frac{c_1 c_2}{M_{12}} \right) & = 1 \quad (2) \\
\beta^\sigma & = \frac{\ln \left( \frac{c_{12}}{X_i^\alpha c_1} \right)}{(1-X_i^\alpha)^2}, \quad (3)
\end{align*}$$

where $X_i$ is the mole fraction of surfactant 1 (OE Isononylphenol) in a complete mixed monolayer; $C_1$, $C_2$ and $C_{12}$ are the molar concentrations in the phases of the solution of surfactant 1, surfactant 2, and their mixture, respectively; $\alpha$ – the mole fraction of surfactant 1 in the mixture. The calculation data are presented in Table 3.

Table 3. Parameters of intermolecular interaction and composition of the adsorption layer for the mixture of OE Isononylphenol and PMD according to the surface tension data

| HLB of the mixed surfactant | $\gamma$, mN/m | $\alpha$ | $X_\sigma$ | $\beta^\sigma$ |
|-----------------------------|----------------|---------|-----------|---------------|
| 6                           | 31,5           | 0,94    | 0,932     | -5,26         |
| 7                           | 31,5           | 0,78    | 0,225     | 2,70          |
| 8                           | 31,5           | 0,62    | 0,283     | 3,25          |
| 9                           | 31,5           | 0,47    | 0,252     | 3,93          |
| 10                          | 31,5           | 0,31    | 0,064     | 4,39          |
| 11                          | 31,5           | 0,16    | 0,033     | 4,73          |
As can be seen from Table 3, the interaction parameter takes negative values only for the HLB of the mixture equals 6. Based on the pseudo-phase separation model [22], the interaction parameter $\beta^m$ and the composition of mixed micelles were calculated. The basis of this approach is the theory of regular solutions. It is believed that the partial entropies of the components in the mixed micelle are equal to the entropies of the ideal micelle, and the enthalpy of mixing is non-zero. The interaction parameter of the pseudo-phase separation model can be calculated by equation (4) and (5):

$$\beta^m = \frac{\ln(a_{12}c_{1m}/c_{2m})}{(1-c_{1m})^2},$$

where $X_{1m}$ is the mole fraction of surfactant 1 in the mixed micelle; $C_{1m}$, $C_{2m}$ and $C_{12m}$ – CMC surfactant 1, surfactant 2, and their mixtures, respectively; $\alpha$ – the mole fraction of surfactant 1 in the total solution of the mixture.

By determining experimentally the CMC values of individual surfactants and their mixtures in the numerical solution of equation (5), finding $X_{1m}$, and substituting the obtained values of $X_{1m}$ in (6) we were able to determine the interaction parameter of the surfactant in mixed micelles (Table 4).

Table 4. Intermolecular interaction parameters and the composition of the adsorption layer for a mixture of OE Isononylphenol and PMD at the water – Vaseline oil interface according to CMC data (HLB mixture = 6)

| System                                             | $\alpha$ | $C_{1m}$ | $C_{2m}$ | $C_{12m}$ | $X_{1m}$ | $\beta^m$ |
|----------------------------------------------------|----------|----------|----------|-----------|----------|-----------|
| H$_2$O – OE Isononylphenol – PMD – Vaseline Oil       | 0,94     | 0,02     | 0,04     | 0,01      | 0,723    | –5,6      |

As a rule, surfactant mixtures do not behave ideally when micelle formation or adsorption on the water / oil interface takes place; synergistic and antagonistic effects are observed. Synergism is manifested in the fact that this value of interfacial tension (or CMC) is achieved at concentrations lower than it was when the components were perfectly mixed.

According to [22–25], the criteria for synergism in micelle formation must be the fulfillment of two conditions:

1. Existence of synergism in the efficiency of reducing the interfacial tension, if the following relations are true:
   1) $\beta^0 < 0$; 2) $|\ln(C_1/C_2)| < |\beta^0|$.
2. The synergism during mixed micelle formation occurs when the CMC of the surfactant mixture has a lower value than the CMC of individual surfactants forming micelles. The fulfillment of the following conditions indicates synergism in mixed micelle formation:
   1) $\beta^m < 0$; 2) $|\ln(C_{1m}/C_{2m})| < |\beta^m|$. For the H$_2$O – OE Isononylphenol – PMD – Vaseline oil system (HLB = 6) all these criteria were observed. This implies that synergism in mixed micelles formed in all systems was existed.

To confirm the above-described assumption about the relationship of the HLB principle and interaction parameter and their influence on the nature of the structures formed, the systems Water – OE Isononylphenol – PMD – Vaseline oil were obtained with a constant composition of water and oil and mass concentrations of the surfactant mixture according to the ratios defined above (Table 1).

Only in the case of HLB = 6, a transparent solution is observed, visually corresponding to the microemulsion, which confirms the approaches described above on the principle of HLB and the interaction parameter (Fig. 3, a). In the mixture with HLB = 7, the start of crystallization process is observed, which corresponds to the pretransition state of microemulsion – liquid crystal (Fig. 3, b). When HLB of mixture equals 8, the hexagonal texture of the mesophase is observed again in the polarization light (Fig. 3, c) [26]. At higher concentrations of PMD (HLB = 9–11) there is crystallization and the system becomes more viscous and pasty (Fig. 3, d).
Thus, by varying the HLB of the surfactant mixture it is possible to control the surfactant – co-surfactant interaction in order to obtain various self-organizing structures such as microemulsions and liquid crystal mesophases.

Conclusion

The interactions of surfactants: OE Isononylphenol and Polyglyceryl-3 Methylglucose Distearate at the water – Vaseline oil interface were investigated. It was shown that they exhibit synergism of action which effects on the decrease the interfacial tension.

The main adsorption characteristics are calculated, the possible orientation of these surfactants at the liquid – liquid interface is shown.

An approach has been proposed for calculating the relation of surfactant – co-surfactant concentrations in a mixture, taking into account the principle of additivity of HLB, measurement of interfacial tension and interaction energy. It was shown that by varying the HLB of surfactant mixture one can influence the self-organization of the surfactant.

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