Adsorption Layer Characteristics of Mixed Oxyethylated Surfactant Solutions

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In the presented work, bubble profile analysis tensiometry is used to study the equilibrium surface tensions and the rheological behavior of solutions of mixed oxyethylated alcohols ($C_{12}EO_5$/$C_{14}EO_8$) and their mixtures with polyethylene glycol octylphenyl ethers (Triton X45/Triton X165). For the analysis of the experimental data, a new theoretical model for mixtures of two nonionic oxyethylated surfactants was employed which assumes two states of surfactant molecules with different molar areas in the surface layer and an intrinsic compressibility of the molecules in the state of closest packing. The theoretical models allow an accurate description of the experimental equilibrium surface tensions for all studied mixed solutions. For the analysis of the rheological behavior of the studied mixed surfactant solutions, the theory for a diffusional adsorption mechanism was applied, and a satisfactory agreement between the experimental data and the calculated viscoelasticity modulus and phase angle was achieved.

Introduction

Studies of surfactant mixtures are of increasing interest from a practical and theoretical point of view.[1−16] In many applications, such as in detergency, foam and emulsion stabilization, painting and coating, and textile finishing, typically, surfactant mixtures are used. This is caused by two events. At first, surfactant mixtures can provide properties to interfaces which any single surfactant cannot, for example, to be adsorbed quickly at an interface on one side and also strongly not to be desorbed during external perturbations. Second, commercial surfactants are, in most cases, mixtures of several compounds, that is, they often contain mixtures of different alkyl chain lengths. Moreover, as is the case with the nonionic C_nEO_m surfactants, they additionally contain ethylene oxide chains of different lengths. Therefore, using different experimental techniques, mixed surfactant adsorption layers have been extensively studied. In refs 17−23, for example, mixtures of nonionic oxyethylated surfactants were systematically investigated.

Until recently, the ideal solution approach and the regular solution theory have formed the basis for understanding surfactant mixing. However, although the number of publications dealing with theories on mixed solutions of nonionic surfactants is quite large, the developed theories did not account for the important adsorption property of oxyethylated surfactants, namely, the dependence of molar area depending on the surface coverage. It was shown recently[24−28] that the adsorption of oxyethylated surfactants solutions is best described by the reorientation model, which assumes that the surfactant molecule can exist at the surface in two orientational states with different molar areas. The agreement with

the experimental data becomes even better if the model assumes additionally a so-called intrinsic compressibility of the adsorbed molecules in the state of closest packing.[29] It was also shown, for example, that all experimental data available for $C_{14}EO_8$ solutions, including dynamic and equilibrium surface tensions, adsorption values, and dilational rheology, can be described in the best possible way by a combined reorientation/compressibility model.[30] This model assumes the ability of the oxyethylene groups to be oriented flat at the solution/air interface at low surface coverage and to point into the solution at increased surface pressure. This reorientation of the EO groups together with the consideration of an intrinsic compressibility of the surface layer in the state of minimum molar area, that is, the change of orientation of the hydrocarbon chains with respect to the interface in the densely packed surface layer, allow a perfect description of any C_nEO_m adsorption layer.[29]

A most rigorous model with respect to the nonideality of entropy of mixed surface layers[25] was used recently for the analysis of surfactant mixtures.[31] In particular, the adsorption behavior of a nonionic oxyethylated surfactant was described by the reorientation/compressibility model, while for the second surfactant in the mixture, a Frumkin-type adsorption model with additional intrinsic compressibility was assumed.

In the present study, the model given in refs 25 and 31 is generalized for the case of mixtures of two surfactants, both of which exhibit reorientation and intrinsic compressibility in the surface layer. For mixtures of the oxyethylated alcohols $C_{14}EO_8$/$C_{12}EO_5$ and of Tritons with different degrees of oxyethylation, it is shown that the proposed model provides a sound description of concentration dependencies of the surface tension and dilation rheology.

Theory

The chemical potentials μ_i^s and μ_i^α of the components in a mixture of different substances in the surface layer (Butler's equation[32])

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$$\mu_i^s = \mu_i^{0s} + RT \ln f_i^s x_i^s - \gamma \omega_i \qquad (1)$$

and in the solution bulk

$$\mu_i^\alpha = \mu_i^{0\alpha} + RT \ln f_i^\alpha x_i^\alpha \qquad (2)$$

lead to the most general equations of state for the surface layer and the adsorption isotherm for the *i*th component (or state).[5,33,34] For ideally dilute solutions, we have from eqs 1 and 2

$$\Pi = -\frac{RT}{\omega_0}(\ln x_0^s + \ln f_0^s) \qquad (3)$$

$$\ln \frac{f_i^s x_i^s / f_{i0}^s}{K_i x_i^\alpha} = \frac{\omega_i}{\omega_0}(\ln x_0^s + \ln f_0^s) \qquad (4)$$

where $\Pi = \gamma_0 - \gamma$ is the surface pressure, γ_0 and γ are the surface tension of solvent and solution, respectively, R is the gas law constant, T is the temperature, f_i are the activity coefficients standardized at $f_i = 1$ and $x_i = 1$, f_{i0} are the activity coefficients at $x_i \to 0$, $x_i = N_i / \Sigma N_i$ are the molar fractions, N_i are the numbers of moles of the *i*th component (or state), ω_i are the molar areas, and K_i are the adsorption equilibrium constants defined at infinite dilution where $\Pi = 0$. The subscript 0 refers to the solvent, the superscript 0 denotes the standard state, and the superscripts s and α indicate the surface layer and bulk phase, respectively. To define the standard state, one usually assumes that the solvent ($i = 0$) is a pure liquid. A better accessible approach for all surface-active component is to assume at that infinite dilution, $x_i^\alpha \to 0$. It should be noted that eqs 3 and 4 were obtained under the condition $\omega_0 = \text{const}$.

The given set of equations allows one to analyze mixed adsorption layers of oxyethylated surfactants. It was mentioned above that the adsorption behavior of an oxyethylated surfactant is best described by the reorientation model which assumes two states of the surfactant molecule in the surface layer.[24−28,30] The dependence of the molar fractions of the components (or of the adsorption states of one surfactant) in the surface layer on the monolayer coverage and the equations for the activity coefficients of the components (which account for the contributions originating from the nonideality of entropy and enthalpy) were derived in refs 5, 34, and 35.

The general relationship between molar surface fractions and area fractions in terms of $n_i = \omega_i / \omega_0$ takes a form[34]

$$x_k^s = \frac{\theta_k}{n_k \sum_{i \geq 0}(\theta_i / n_i)} \qquad (5)$$

Equation 5 is used to express eqs 3 and 4 via the surface area fractions $\theta_i = \omega_i \Gamma_i$ instead of the molar fractions x_i^s. The following expressions for the entropic contribution to the activity coefficients according to Lucassen-Reynders should be used[34,35]

$$\ln f_j^{sE} = 1 - n_j \sum_{i \geq 0}(\theta_i / n_i) + \ln[n_j \sum_{i \geq 0}(\theta_i / n_i)] \qquad (6)$$

Using the regular solution theory, the activity coefficients determined by intermolecular interactions (enthalpic nonideality,

f_i^{sH}) can be calculated.[5] In particular, for f_0^{sH} in a solution of two surfactants, we have

$$\ln f_0^{sH} = a_1 \theta_1^2 + a_2 \theta_2^2 + 2a_{12} \theta_1 \theta_2 \qquad (7)$$

where a_{ij} are the constants of interaction between the species in the surface layer.

The additivity of the enthalpy and entropy terms in the Gibbs free energy results in

$$\ln f_i^s = \ln f_i^{sH} + \ln f_i^{sE} \qquad (8)$$

In this study, we assumed an ideal behavior with respect to the enthalpy of surfactants in the individual adsorption layers ($a_1 = 0$ and $a_2 = 0$) and used only one interaction parameter $a = a_{12}$ for the mixtures in order to reduce the number of parameters in the present theoretical model. By introducing respective expressions for f_0^s and x_0^s into eq 3 and using the approximation $\omega_{10} \cong \omega_{20}$ for the two reorientable surfactants 1 and 2, the following equation of state for the mixed adsorption layer was obtained

$$-\frac{\Pi \omega_0^*}{RT} = \ln(1 - \theta_1 - \theta_2) + \theta_1(1 - \omega_{10}/\omega_1) + \theta_2(1 - \omega_{20}/\omega_2) + 2a\theta_1\theta_2 \qquad (9)$$

with

$$\omega_0^* = \frac{\omega_{10}\theta_1 + \omega_{20}\theta_2}{\theta_1 + \theta_2} \qquad (10)$$

where $\theta_i = \omega_i \Gamma_i$ is the surface coverage by surfactant molecules of component i ($i = 1$ or 2), Γ_i is the adsorption, ω_{i0} is the molar area in the states of minimum area at zero surface pressure, and a is the constant of interaction between surfactant molecules 1 and 2. The total adsorption consists of the amounts of surfactant adsorbed in two states, $\Gamma_1 = \Gamma_{11} + \Gamma_{12}$ and $\Gamma_2 = \Gamma_{21} + \Gamma_{22}$. Here and in the following discussion, the first subscript refers to the surfactant and the second to the state of the surfactant at the surface. The molar areas of surfactants adsorbed in states 1 and 2 are denoted by ω_{i1} and ω_{i2} (to be definite, we assume $\omega_{i2} > \omega_{i1}$); hence, the partial coverages of the monolayer are $\theta_i = \omega_i \Gamma_i = \omega_{i1}\Gamma_{i1} + \omega_{i2}\Gamma_{i2}$.

As proposed in ref 36, the molar areas of the surfactants (in the states of minimum area) can be approximated by a linear dependence on the surface pressure Π and total surface coverage $\theta = \theta_1 + \theta_2$

$$\omega_{11} = \omega_{10}(1 - \varepsilon_1 \Pi \theta) \qquad (11)$$

$$\omega_{21} = \omega_{20}(1 - \varepsilon_2 \Pi \theta) \qquad (12)$$

Here, the parameters ε_i are the two-dimensional relative surface layer compressibility coefficients which characterize the intrinsic compressibility of molecules in the surface layer.[29]

Using eq 4 and the expressions for the molar fractions x_i given by eqs 5 and activity coefficients f_i of eqs 6−8 derived in refs 5, 34, and 35, one obtains the adsorption isotherms for the mixture

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components and their states. For the states 11 and 12 of surfactant 1, the adsorption isotherms read

$$b_1 c_1 = \frac{\Gamma_{11}\omega_{10}}{(1-\theta)^{\omega_{11}/\omega_{10}}} \exp(-2a\theta_2) \qquad (13)$$

$$b_1 c_1 = \frac{\Gamma_{12}\omega_{10}}{(\omega_{12}/\omega_{11})^{\alpha_1}(1-\theta)^{\omega_{12}/\omega_{10}}} \exp(-2a\theta_2) \qquad (14)$$

while for the states 21 and 22 of surfactant 2, we have

$$b_2 c_2 = \frac{\Gamma_{21}\omega_{20}}{(1-\theta)^{\omega_{21}/\omega_{20}}} \exp(-2a\theta_1) \qquad (15)$$

$$b_2 c_2 = \frac{\Gamma_{22}\omega_{20}}{(\omega_{22}/\omega_{21})^{\alpha_2}(1-\theta)^{\omega_{22}/\omega_{20}}} \exp(-2a\theta_1) \qquad (16)$$

Here, b_i are the adsorption equilibrium constants, c_i are the surfactant bulk concentrations, and α_i are the power law exponents.[25]

Therefore, the ratios of the adsorptions in states 1 and 2 for the two reorientable surfactants ($i = 1$ and 2) are given by

$$\frac{\Gamma_{i1}}{\Gamma_{i2}} = \frac{1}{(\omega_{i2}/\omega_{i1})^{\alpha_i}(1-\theta)^{(\omega_{i2}-\omega_{i1})/\omega_{i0}}} \qquad (17)$$

Note, the only additional model parameter for the mixture is the constant a, which describes the intermolecular interaction between the molecules of different species while all other model parameters refer to the individual solutions. If only one of the two components of the mixture is present in the solution, the given set of equations becomes identical to the model developed earlier for single reorientable surfactants regarding the nonideality of entropy of the surface layer and the intrinsic compressibility of adsorbed surfactant molecules.[36]

The procedure used for the numerical calculations is quite straightforward; given the known values of T, ω_{10}, ω_{12}, ω_{20}, ω_{22}, α_1, α_2, a, ε_1, ε_2, b_1, and b_2, for any given values of the surfactant concentrations c_1 and c_2, the values of θ_1 and θ_2 can be calculated via eqs 13–17. These θ_1 and θ_2 values are then used to calculate the adsorption values $\Gamma_1 = \Gamma_{11} + \Gamma_{12}$ and $\Gamma_2 = \Gamma_{21} + \Gamma_{22}$, and finally, the surface pressure Π is obtained via eqs 9 and 10.

Experimental Section

The experiments were performed with the bubble/drop profile analysis tensiometer PAT (SINTERFACE Technologies, Germany), the principle of which was described in detail elsewhere.[37,38] The temperature of the measuring cell with a volume of $V = 20$ mL was kept constant at 25 °C. In this study, we used a buoyant bubble formed at the bottom tip of a vertical Teflon capillary with a diameter of 3 mm. It should be noted that for studies of surfactant mixtures of different adsorption activity, one has to employ the bubble rather than the drop profile method in order to have a large volume to surface area ratio. This ensures that the adsorption of neither of the surfactants at the interface depletes the bulk concentration.[39]

To study the dilational viscoelasticity E, after having reached the adsorption equilibrium, the bubble was subjected to harmonic
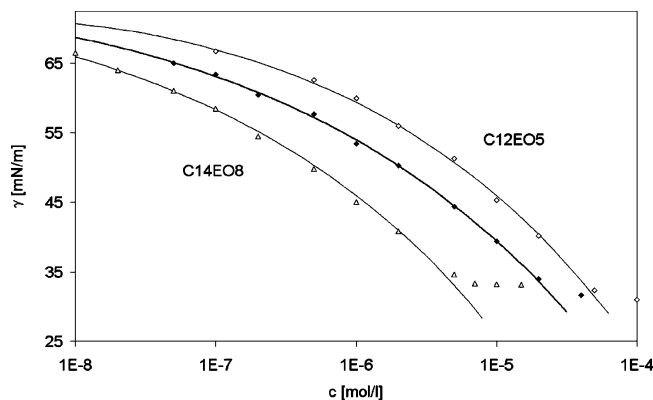

Figure 1. Dependence of the equilibrium surface tension γ on concentration c for individual solutions of $C_{12}EO_5$ ($\diamond$) and $C_{14}EO_8$ ($\triangle$) and for $C_{12}EO_5/C_{14}EO_8$ mixtures at a molar ratio of 3:1 ($\blacklozenge$). Theoretical curves were calculated with the proposed model using the parameters given in the text.

oscillations at frequencies between 0.005 and 0.2 Hz and surface area oscillation amplitudes of 5–7%. The results of these harmonic relaxation experiments were analyzed using a Fourier transformation[37]

$$E(i\Omega) = A_0 \frac{F[\Delta\gamma]}{F[\Delta A]} \qquad (18)$$

where A_0 is the initial area of the bubble surface, γ is the surface tension, and Ω is the angular frequency of generated oscillations.

The oxyethylated alcohols $C_{14}EO_8$ and $C_{12}EO_5$ were purchased from Sigma Chemical and used without further purification. Polyethylene glycol octylphenyl ethers, $C_{14}H_{21}O(C_2H_4O)_nH$ (Tritons X-45, X-100, and X-165, with $n \approx 5$, 10, and 16, respectively) from Sigma Chemical were also used without further purification. The solutions were prepared using Milli-Q water. The surface tension of this water was 72.0 ± 0.2 mN/m at 25 °C over a time interval of up to 10^5 s (about 28 h).

Results and Discussion

Figure 1 shows the experimental equilibrium surface tension isotherm γ as a function of the total concentration c for mixed $C_{12}EO_5/C_{14}EO_8$ solutions taken at a ratio of 3:1. To attain the equilibrium surface tensions, adsorption times of 15000 (dilute solutions) or 2000 s (concentrated solutions) were required. Shown in Figure 1 are also the experimental surface tension isotherms of the individual solutions of $C_{12}EO_5$ and $C_{14}EO_8$, as reported in ref 31. The theoretical isotherms for the two surfactants were calculated from for the rigorous reorientation model (where the nonideality was accounted for), as derived in ref 36. It was mentioned above that for single surfactants, the set of eqs 9–17 becomes identical to the equations presented in ref 36. The reorientation model parameters for the oxyethylated surfactants studied here are listed below. For the sake of clarity the subscripts correspond to the notation above, that is, "1" for $C_{12}EO_5$ and "2" for $C_{14}EO_8$.

$C_{12}EO_5$: $\omega_{10} = 4.2 \times 10^5$ m²/mol, $\omega_{12} = 1.0 \times 10^6$ m²/mol, $\alpha_1 = 2.5$, $\varepsilon_1 = 0.006$ m/mN, $b_1 = 5.1 \times 10^3$ m³/mol.

$C_{14}EO_8$: $\omega_{20} = 5.7 \times 10^5$ m²/mol, $\omega_{22} = 1.0 \times 10^6$ m²/mol, $\alpha_2 = 2.8$, $\varepsilon_2 = 0.007$ m/mN, $b_2 = 1.0 \times 10^5$ m³/mol.

As one can see, the surface activity of $C_{14}EO_8$ (constant b_2) is by more than 1 order of magnitude higher, than the activity of $C_{12}EO_5$ (constant b_1). The corresponding theoretical isotherm for a 3:1 mixture of $C_{12}EO_5/C_{14}EO_8$ for $a = 0$ is also shown in
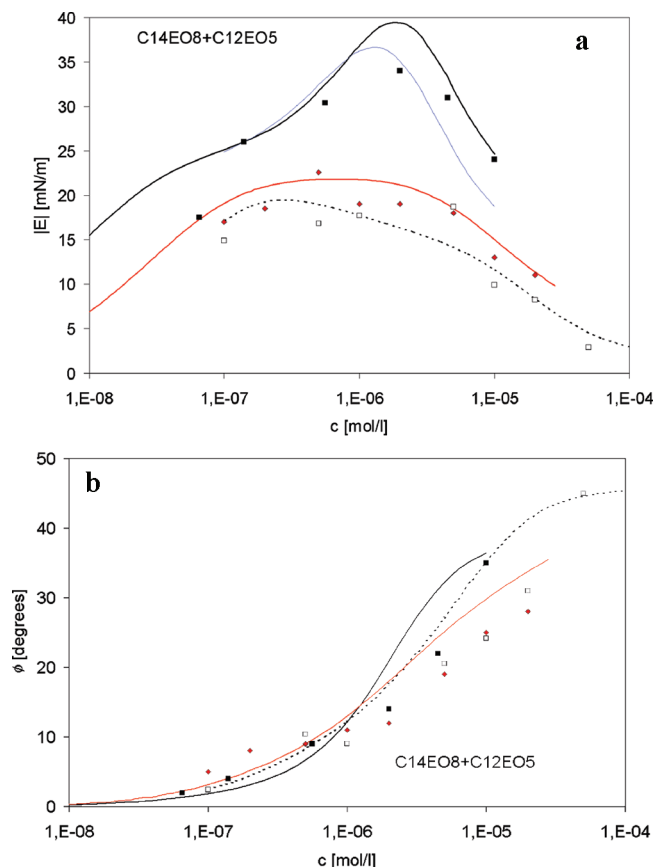
Figure 2. Dependence of the viscoelasticity modulus $|E|$ (a) and phase angle ϕ (b) on concentration c at an oscillation frequency of 0.01 Hz for individual $C_{12}EO_5$ ($\square$, dotted curve) and $C_{14}EO_8$ ($\blacksquare$, solid curve) solutions and 3:1 $C_{12}EO_5/C_{14}EO_8$ mixtures (red $\blacklozenge$, red curve); calculated for $C_{14}EO_8$ with $D = 10^{-9}$ m²/s (thin blue line); points, experimental data; lines, calculated dependencies.

Figure 3. (a, b) The same as in Figures 2 for an oscillation frequency of 0.1 Hz.

Figure 1. It is seen that the use of the given parameters of the individual solutions provides a perfect agreement with the experimental data. Note, by using these parameters, also the adsorption values $\Gamma(c)$ for the individual solutions were calculated. Comparing the calculated results with the data directly measured by neutron reflection,[11] we find good agreement.[31]

The experimental dependencies of the viscoelasticity modulus $|E|(c)$ and phase angle $\phi(c)$ in a wide range of $C_{12}EO_5$ and $C_{14}EO_8$ concentrations were obtained by using the buoyant bubble profile method involving harmonic oscillations of the bubble area. Figure 2a and b illustrates the experimental dependencies of the viscoelasticity modulus and phase angle, respectively, on the concentration of $C_{12}EO_5$, $C_{14}EO_8$, and the $C_{12}EO_5/C_{14}EO_8$ mixture (ratio 3:1) at a frequency of 0.01 Hz. The corresponding dependencies for a second frequency of 0.1 Hz are shown in Figure 3a and b. The data for the individual $C_{12}EO_5$ and $C_{14}EO_8$ solutions shown in Figures 2 and 3 are reproduced from ref 40. For all studied solutions, the viscoelasticity modulus exhibits a maximum, while the phase angle increases monotonously with the surfactant concentration.

For the analysis of the experimental data of the $C_{12}EO_5/C_{14}EO_8$ mixture, the theoretical approach proposed in ref 41 was employed, which describes the dilational rheology of the mixtures of two surfactants with a diffusional adsorption mechanism. To determine the six partial derivatives in the expressions for the surface viscoelastic properties, we have to assume a ce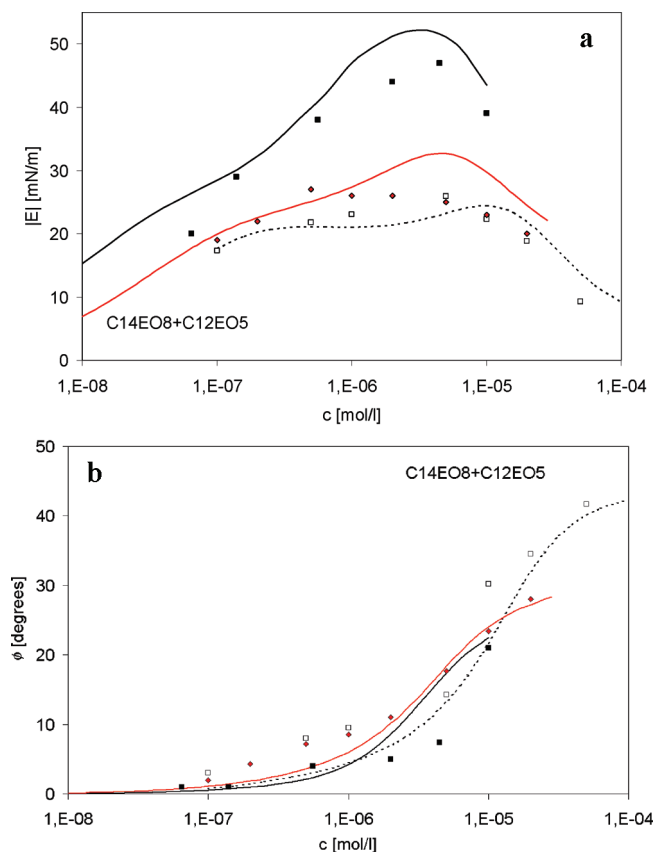rtain surface layer model which obeys respective equations of state and adsorption isotherms. In the present case, the model is defined by eqs 9−17. The additional parameters relevant for the analysis of the rheological behavior are the diffusion coefficients (D_i) of the mixture components. The best agreement between the calculated results and the experimental values was obtained for $D = 10^{-9}$ m²/s for both components, which is physically quite realistic. Note, in ref 40, for the fitting of the rheological data for the same surfactants, a value of $D = 5 \times 10^{-10}$ m²/s was used, which is quite close to that indicated above. The corresponding curves for this value of D are also shown in Figures 2 and 3. However, this small difference in the diffusion coefficients only slightly affects the curves. As an example, the dependence of the elasticity modulus for $C_{14}EO_8$ with $D = 10^{-9}$ m²/s is shown by a thin (blue) line in Figure 2a.

The comparison between the experimental dependencies of the elasticity modulus and phase angle on the total concentration of the $C_{12}EO_5/C_{14}EO_8$ mixtures and the results calculated from eqs 9−17 and the model given in 41 provides good agreement.

Let us consider now the mixtures of Triton X-45/Triton X-165 (TX45/TX165) at a mixing ratio of 1:1. This mixing ratio was taken because the resulting surface-active substance would approximately correspond to Triton X-100 (TX100), that is, the average number of oxyethylene groups for this mixture is about 10, although their distribution (polydispersity) for this "artificial" mixture is significantly wider than that of TX100.

The equilibrium surface tension isotherms for TX45, TX165, and TX100 reproduced from ref 36 are shown in Figure 4 along with the experimental isotherms for the 1:1 TX45/TX165 mixture of the present study. One can see that the isotherm for the TX45/TX165 mixture is quite close to that of TX100, and the most significant deviations (up to 3 mN/m) are observed only at very low and very high concentrations. In the region,
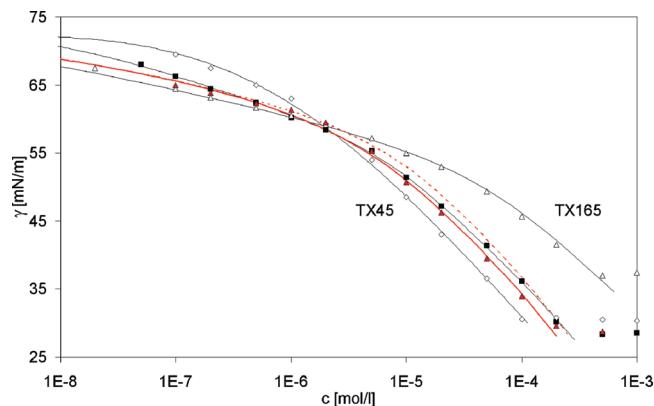
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Figure 4. Dependence of the equilibrium surface tension γ on concentration c for individual solutions of TX45 ($\diamond$), TX165 ($\triangle$), and TX100 ($\blacksquare$) and for 1:1 TX45/TX165 mixtures ($\blacktriangle$). Theoretical curves were calculated with the proposed model using the parameters given in the text. The solid red curve was calculated for the TX45/TX165 mixture with $a = 0.7$; the red dotted curve corresponds to $a = 0$.

which corresponds to the concentration below the point of intersection of all isotherms for Tritons, the values obtained for the TX45/TX165 mixture become closer to those obtained for the pure TX165, while for the concentrations above this point, the values move closer to those for pure TX45. Note that an intersection of all isotherms is observed at a concentration of about 1 μmol/L and a surface tension of about 60 mN/m.[36] For concentrations below this intersection point, the surface activity of Tritons with longer oxyethylene chains is higher, which should be ascribed to the partial adsorption of the oxyethylene groups. On the contrary, for higher concentrations, the Tritons with shorter oxyethylene chains (and therefore less hydrophilicity) exhibit higher surface activity. It can be assumed that this is the wider distribution of the oxyethylated groups in the studied TX45/TX165 mixture which influences the surface tension such that the component with the long oxyethylene chain is dominant at low concentrations, while for high concentrations, the effect of the components with the short EO chain is stronger.

The theoretical surface tension isotherms for the TX45, TX165, and TX100 solutions were calculated earlier in ref 36. To calculate the surface tension isotherm for the TX45/TX165 mixture, the values of the parameters of the rigorous reorientation model for the individual solutions given in ref 36 were used.
TX45: $\omega_{10} = 3.8 \times 10^5$ m²/mol, $\omega_{12} = 6.0 \times 10^5$ m²/mol, $\alpha_1 = 0$, $\varepsilon_1 = 0.007$ m/mN, $b_1 = 1.39 \times 10^3$ m³/mol.
TX165: $\omega_{20} = 5.0 \times 10^5$ m²/mol, $\omega_{22} = 1.5 \times 10^6$ m²/mol, $\alpha_2 = 6.0$, $\varepsilon_2 = 0.006$ m/mN, $b_2 = 1.77 \times 10^3$ m³/mol.

Figure 4 shows two theoretical curves calculated for the 1:1 TX45/TX165 mixture; the dotted red line corresponds to the model parameters listed above and $a = 0$, while the solid red line was obtained by fitting the parameter a. The best fit value is $a = 0.7$. Presumably, this value is caused by the preferential contribution to the mixture properties from the components with the smaller number of oxyethylene groups at high concentrations.

Figures 5a, b and 6a, b illustrate the experimental dependencies of the viscoelasticity modulus and phase angle on the concentration of TX45, TX165, and the 1:1 TX45/TX165 mixtures at a frequency of 0.01 and 0.1 Hz, respectively. The shown theoretical and experimental dependencies for the individual TX45 and TX165 solutions are reproduced from ref 42. For the sake of comparison, in Figures 5a and 6a, the experimental values of the elasticity modulus for TX100 are also shown. One can see that these values are quite close to the experimental results for the mixture.
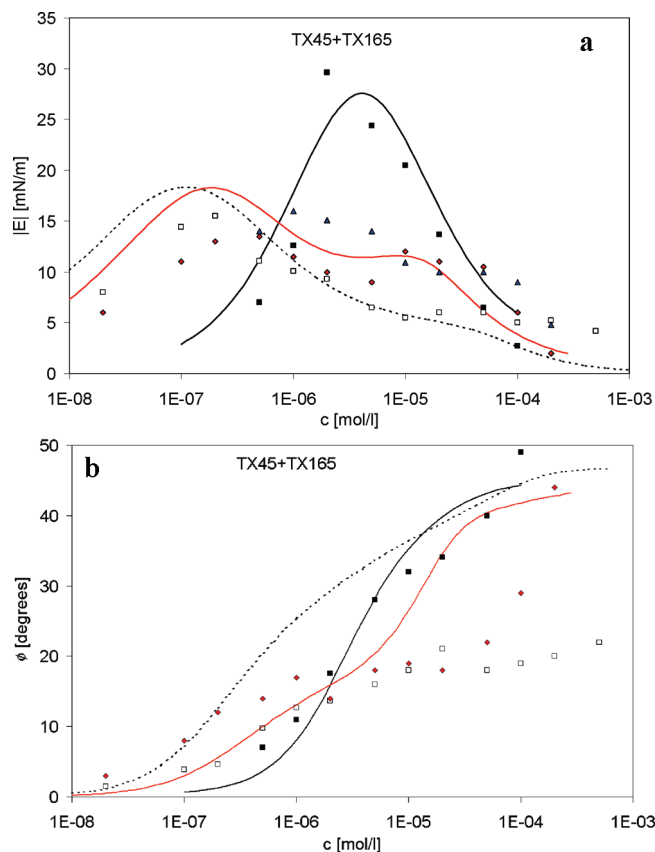

Figure 5. Dependence of the viscoelasticity modulus $|E|$ (a) and phase angle ϕ (b) on concentration at an oscillation frequency of 0.01 Hz for individual TX45 ($\blacksquare$, solid curve) and TX165 ($\square$, dotted curve) solutions and 1:1 TX45/TX165 mixtures (red $\blacklozenge$, red curve). Blue $\blacktriangle$ are data for TX100. Points, experimental data; lines, calculated dependencies.

The theoretical dependencies in Figures 5 and 6 were calculated via eqs 9−17 using the model developed in ref 41. Similarly to the individual Triton solutions,[36] the diffusion coefficient for both components was taken to be $D = 3 \times 10^{-10}$ m²/s, which leads to a quite good agreement between theory and experiment, especially the for the viscoelasticity modulus $|E|(c)$. Moreover, the calculated $|E|(c)$ curves for the mixture reproduce very well the particularities of the experimental dependencies, for example, the presence of two maxima in the $|E|(c)$ dependencies (Figures 5a and 6a); however, the agreement for the phase angle ϕ is mainly qualitative (Figures 5b and 6b). It was shown in ref 42 that the first maximum is caused by the transition of the expanded state of the adsorbed Triton molecules in the surface layer (ethylene oxide groups are partially adsorbed at the interface) to a more compact state (increase in surface pressure leads to the desorption of the ethylene oxide groups from the interface). This phenomenon becomes apparent for long oxyethylene chains. In our case, this behavior is observed for the individual TX165 and TX45/TX165 mixed solutions. The existence of the second maximum in concentrated solutions (at sufficiently low oscillation frequencies) is caused by a diffusional exchange between the solution bulk and surface layer and the intrinsic compressibility of the Triton molecules at high surface pressure.

Conclusions

In the presented work, bubble profile analysis tensiometry is used to study the equilibrium surface tensions and the rheological behavior of mixed $C_{12}EO_5/C_{14}EO_8$ and TX45/TX165
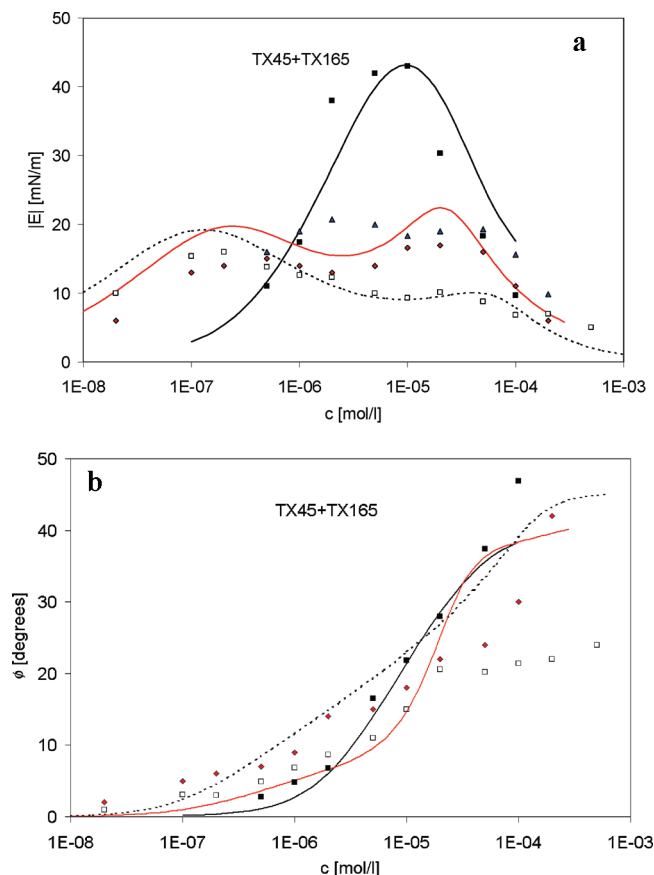
Figure 6. (a, b) The same as in Figures 5 for the oscillation frequency of 0.1 Hz.

solutions. For the analysis of the experimental data, a new theoretical model for mixtures of two nonionic oxyethylated surfactants was employed which assumes two adsorption states with different molar areas in the surface layer and an intrinsic compressibility of the molecules in the state of minimum area. The theoretical models allow an accurate description of the experimental results for the equilibrium surface tensions of all studied mixed solutions. For the analysis of the rheological behavior of the mixed solutions, a theoretical approach was employed, which describes the dilational rheology of binary surfactant mixtures for a diffusional exchange of matter mechanism.[41] This approach requires a refinement of the equations of state of the mixed surface layer and the corresponding adsorption isotherms. A satisfactory agreement between the experimental data and the calculations of the viscoelasticity modulus and phase angle was achieved.

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