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Equilibrium and dynamic surface properties of trisiloxane aqueous solutions.

Part 2. Theory and comparison with experiment

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Abstract

In the first part of this paper we presented experimental results, which shows the presence of surface aggregates in aqueous solutions of trisiloxane surfactants (Hernan A. Ritacco, Francisco Ortega, Ramon G. Rubio, Natalia Ivanova and Victor M. Starov. Equilibrium and dynamic surface properties of trisiloxane aqueous solutions. Part 1. Experimental results). Formation of those aggregates has been found for those trisiloxanes (T6, T7, T8, and T9), which show superspreading behaviour at room temperature. However, the formation of surface aggregates has not been detected for trisiloxanes (T4 and T5), which do not show superspreading behaviour at room temperature. It is shown that experimental results on equilibrium and dynamic interfacial tension agree well with a combined theoretical model, which is based on reorientation (or two-state) and aggregation models. According to the reorientation model there are two states of trisiloxane molecules on the surface layer: molecules in those two states occupy different surface area. The aggregation model was modified to account for specific properties of trisiloxane molecules. According to that model molecules occupying the lowest area on the interface can form two dimensional aggregates. It was assumed that trisiloxanes molecules include two kinetically independent trimethylsilyl [$-O-Si(CH_3)_3$] groups. This assumption allowed us to agree the aggregation theoretical model and experimental data on ellipsometric measurement of adsorption.

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Introduction

In [1] equilibrium and dynamic surface tension of aqueous solutions of trisiloxanes surfactants as well as adsorption of trisiloxane molecules at liquid-air interface were measured by tensiometry, ellipsometry and Brewster angle. It was found that trisiloxane surfactants with relatively long hydrophilic chains (number of oxyethylene units N>6) at concentration above a certain value form surface aggregates. The latter means that the surfactant molecules are present at the liquid-vapour interface in two states. We have associated one of the states to surfactant as being adsorbed as a monomer, and the other corresponding to the surfactant adsorption as a part of a surface aggregate. These surface aggregates could act as reservoirs of surfactant monomers in the course of spreading. Below we present a theoretical model, which allows us to describe reasonably well the previous experimental findings.

Existing theoretical models

Reorientation model

Reorientation model (or two-state model) describes well adsorption behaviour of different oxyethylene surfactants on liquid-air interfaces [2-6]. At low surface concentrations both carbohydrate and oxyethylene groups of those surfactants adsorb simultaneously. As a result the area per surfactant molecule on the interface reaches the maximum values. On the contrary, at higher surface concentrations only carbohydrate groups are capable to adsorb and, hence, the area per molecule at the interface decreases. Trisiloxane surfactant molecules used in our experiments have from 4 to 9 oxyethylene groups. That is, adsorption of those surfactants experimentally investigated in the first part[1] should also well be described by the above model. The theoretical two states models were used to describe the equilibrium surface tension and adsorption of surfactants and were described in earlier elsewhere [6,7-10]. Therefore, only the main equations for each applied model are given below.

The reorientation model assumes that two orientations of adsorbed surfactant molecules coexist at the surface, with different molar areas ω_1 and ω_2 (for definiteness we assume $\omega_2 > \omega_1$). Assuming ideal enthalpy of mixing of the surface layer, the equations of state and adsorption isotherm read [7-9]:

$$\Pi = -\frac{RT}{\omega}\ln(1-\theta),\qquad(1)$$

$$bc = \frac{\Gamma_1\omega}{(1-\theta)^{\omega_1/\omega}},\qquad(2)$$

where R is the ideal gas constant, T is the absolute temperature, c is the concentration of the surfactant in the bulk solution, $b=b_1$ is the adsorption equilibrium constant in the state 1, ω is the mean area of adsorbed surfactant molecule, $\Pi = \gamma_0 - \gamma$ is the surface pressure, γ_0 and γ are the surface tension of water and surfactant solution, and $\theta = \omega\Gamma$ is the surface coverage. The total adsorption Γ and mean molar area ω are defined as

$$\Gamma = \Gamma_1 + \Gamma_2,\qquad(3)$$

$$\omega\Gamma = \theta = \omega_1\Gamma_1 + \omega_2\Gamma_2.\qquad(4)$$

The ratio of adsorptions in the two possible states of the adsorbed molecules is given by

$$\frac{\Gamma_2}{\Gamma_1} = \exp\left(\frac{\omega_2-\omega_1}{\omega}\right)\left(\frac{\omega_2}{\omega_1}\right)^{\alpha}\exp\left[-\frac{\Pi(\omega_2-\omega_1)}{RT}\right].\qquad(5)$$

The constant α accounts for the fact that the adsorption equilibrium constant b_2 for surfactant molecules adsorbed in state 2 (with larger area) can exceed that in state 1, which results in an additional (as compared to $\alpha = 0$) increase of the fraction of states of larger area. For $\alpha = 0$ the adsorption equilibrium constants b in state 1 and 2 are identical.

In [10] a new advanced reorientation model was suggested which, in contrast to the model discussed above, assumes the non-ideality of both enthalpy and entropy of the mixed adsorption layer. Note, that the non-ideality of entropy is caused by difference of molar area of two states of molecules in the layer.

The surface equation of state according to [10] is as follows:

$$-\frac{\Pi\omega_0}{RT} = \ln(1-\Gamma\omega) + \Gamma(\omega-\omega_0) + a(\Gamma\omega)^2,\qquad(6)$$

where ω_0 is the molar area of the surfactant in state 1 at $\Pi = 0$ (if a compressibility of those surfactant molecules in that particular state is taken into account) [6] or the molar area of the solvent. The total adsorption Γ and mean molar area ω are defined by Eqs. (3) and (4) above.

The adsorption isotherms for the states 1 and 2 are respectively:

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$$bc = \frac{\Gamma_1 \omega_0}{(1-\Gamma\omega)^{\omega_1/\omega_0}} \exp\left(-\frac{\omega_1}{\omega_0}(2a\Gamma\omega)\right), \tag{7}$$

$$bc = \frac{\Gamma_2 \omega_0}{(\omega_2/\omega_1)^{\alpha}(1-\Gamma\omega)^{\omega_2/\omega_0}} \exp\left(-\frac{\omega_2}{\omega_0}(2a\Gamma\omega)\right). \tag{8}$$

The ratio of adsorptions in the two possible states of the adsorbed molecules is expressed by a relation, which can be deduced using Eqs. (7) and (8):

$$\frac{\Gamma_1}{\Gamma_2} = \frac{(\omega_1/\omega_2)^{\alpha}}{(1-\Gamma\omega)^{(\omega_2-\omega_1)/\omega_0}} \exp\left(-\frac{(\omega_2-\omega_1)}{\omega_0}(2a\Gamma\omega)\right). \tag{9}$$

It was shown for several examples that the two reorientation models discussed above provide a good description for the adsorption behaviour of oxyethylated surfactants [10].

Aggregation of adsorbed molecules

It has been shown in [1], that aqueous solutions of trisiloxane surfactants with a number N of oxyethylene groups from 6 to 9 form two dimensional aggregates on a liquid –air interface at concentrations above a critical bulk concentration (at surface pressure above 20 mN/m). We can conclude from Eqs. (5) and (9) that at such surface pressures $\Gamma_1 >> \Gamma_2$. Hence, in this range we can neglect the adsorption in the state 2 and investigate adsorption behaviour of trisiloxanes using already know earlier theoretical models of aggregation processes [10-23].

In [9,20-23] such kind of phase transitions were treated using the quasi-chemical approach based on the analysis of chemical potentials of the components in the surface layer. When aggregates are formed at the surface (interface), the equilibrium between monomers and n-mers can be described by the following equation [9, 20]:

$$\mu_n^s = n\mu_1^s, \tag{10}$$

where $\mu_i^s = \mu_i^{0s} + RT\ln f_i^s x_i^s - \gamma\omega_i$ are the chemical potentials of monomers (i=1) and n-mers (i=n) in surface layer, $\mu_i^{0s}(T,P)$ are the standard chemical potentials, $x_i = m_i/\Sigma m_i$ are the molar fractions, and m_i are the numbers of moles of the ith component, ω_i are the partial molar areas, and f_i are the activity coefficients. Assuming an ideal mixing one can transform Eq. (10) as

$$x_n^s = K_n \left(x_1^s\right)^n \exp(\Pi\Delta\omega/RT), \tag{11}$$

where $K_n = \exp\left\{\left[\left(n\mu_1^o - \mu_n^o\right) - \gamma_0\Delta\omega\right]/RT\right\}$ is the aggregation constant, and $\Delta\omega = n\omega_1 - \omega_n$. The adsorption of aggregates (n-mers) is described by the following relationship:

$$\Gamma_n = K_n \Gamma_1^n \omega^{n-1} \exp(\Pi\Delta\omega/RT). \tag{12}$$

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Assuming that the molar area (per one monomer) remains constant during the aggregation process ($\Delta\omega = 0$, and $\omega_n/\omega_1 = n$) and introducing a critical aggregation adsorption Γ_c (i. e. the value of the adsorption of the monomers which corresponds to the aggregation threshold), the expression for the aggregation constant K_n can be simplified to

$$K_n = \Gamma_c^{-(n-1)}\omega^{-(n-1)},$$ (13)

where ω is the mean molar area of monomers and aggregates, and Eq. (12) for the adsorption of aggregates becomes

$$\Gamma_n = \Gamma_1\left(\frac{\Gamma_1}{\Gamma_c}\right)^{n-1}.$$ (14)

Assuming non-ideal entropy and ideal enthalpy of mixing, the equation of state for surface layers of surfactants forming 2D aggregates is given by the following equation [23]:

$$\Pi = -\frac{RT}{\omega_1}\left[\ln\left[1-\omega_1\Gamma_1\left(1+n\left(\frac{\Gamma_1}{\Gamma_c}\right)^{n-1}\right)\right]+\omega_1 n\Gamma_1\left(\frac{\Gamma_1}{\Gamma_c}\right)^{n-1}\left(1-\frac{1}{n}\right)\right]$$ (15)

The adsorption isotherm of monomers under the same conditions is according to [23]:

$$bc = \frac{\Gamma_1\omega_1}{\left[1-\Gamma_1\omega_1\left(1+n(\Gamma_1/\Gamma_c)^{n-1}\right)\right]}.$$ (16)

The simplified equations can be obtained if the entropic contribution is neglected. Then the equation of state for surface layers of aggregating surfactants and the adsorption isotherm of monomers becomes [9, 2-22]:

$$\Pi = -\frac{RT}{\omega}\ln\left[1-\Gamma_1\omega\left(1+\left(\frac{\Gamma_1}{\Gamma_c}\right)^{n-1}\right)\right],$$ (17)

$$bc = \frac{\Gamma_1\omega}{\left[1-\Gamma_1\omega\left(1+(\Gamma_1/\Gamma_c)^{n-1}\right)\right]^{\omega_1/\omega}},$$ (18)

where the mean molar area of monomers and aggregates ω is defined by

$$\omega = \frac{\Gamma_1\omega_1+\Gamma_n\omega_n}{\Gamma_1+\Gamma_n} = \omega_1\frac{1+n(\Gamma_1/\Gamma_c)^{n-1}}{1+(\Gamma_1/\Gamma_c)^{n-1}}.$$ (19)

For the formation of large aggregates, so-called clusters ($n \gg 1$), the approximations $\Gamma_1 \cong \Gamma_c$ and $1+(\Gamma_1/\Gamma_c)^{n-1} \cong 1$ are valid.[20-22]

Dynamic surface tension and adsorption

The dynamic of adsorption is described by well-known integro-differential equation derived by Ward and Tordai [24]. This equation gives a relationship between the dynamic adsorption, $\Gamma(t)$, and the subsurface concentration $c(0,t)$ for a fresh non-deformed surfaces:

$$\Gamma(t) = 2\sqrt{\frac{D}{\pi}}\left[c_0\sqrt{t} - \int_0^{\sqrt{t}} c(0, t-t')d\sqrt{t'}\right], \tag{20}$$

where D is the diffusion coefficient, c_0 is the bulk concentration, t is time, t' is a dummy integration variable. For the diffusion adsorption mechanism, the relationship between the dynamic adsorption and subsurface concentration is given by the adsorption isotherm equation. If the dynamic surface tension of a surfactant aggregating in the surface layer is studied, then above the critical adsorption of aggregates formation one should expect retardation of the surface pressure dependence on time expressed by the dynamic curve [16,21]. The dynamic curves calculated assuming the aggregation in the monolayer exhibit (for the not too large values of Π) sharp inflection behaviour. The position of the inflection point depends on Γ_c value. The higher is the Γ_c value, the higher are the time and surface pressure values which correspond to the inflection point at the dynamic surface pressure curve [25].

Eq. (20) can also be used for calculations of dynamic surface tension on time for concentrated solutions of trisiloxane surfactants (concentrations above CAC or even CWC) if combined with the theory developed by Joos [26,27]. The theory still assumes that only monomers adsorb at the interface. However, above CAC the monomers at the subsurface have two origins: on one side the diffusion of monomers from bulk, and on the other side the diffusion of aggregates from bulk to the subsurface where they disintegrate because the monomer concentration is lower than the CAC. Assuming that the disintegration process of the bulk aggregates is comparatively fast, it is possible to describe the adsorption of monomers at the air/liquid interface as a single effective process which an effective diffusion coefficient D^* of monomers given by [26,27]:

$$D^* = D(1+\beta)(1+\lambda\beta), \tag{21}$$

where $\lambda = D_m/D \approx 0.25$, $\beta = (c_0 - c_k)/c_k$, $c_k = CAC$, c_0 is the total surfactant concentration, D and D_m are the diffusion coefficients of surfactant monomers and bulk aggregates, respectively. Thus, for the description of the dynamic surface tension of concentrated solutions we have to assume that $c_0 = CAC$ for $c_0 > CAC$, and instead of the value of D for monomers we should use an effective diffusion coefficient D^* for the monomers. Eq. (21) has been recently used by Feinerman et al. to describe the surface behavior of SDS solutions [28].

Results and Discussion

Isotherms of equilibrium surface tension of trisiloxane solutions T6, T7, T8 and T9 presented in [1] are well described using the two stage model (Eqs (1)-(5)). The model parameters are presented in the Table.

Table. Best fitting parameters for the two-states model for TN (N≥6). For T4 and T5 the values shown correspond to the Szyskowski equation.

Trisiloxane	ω_2/ m² mol⁻¹	ω_1/ m² mol⁻¹	α	b/ m³ mol⁻¹
T4	–	3.2×10^5	–	2.5×10^4
T5	–	3.1×10^5	–	4.2×10^4
T6	7.6×10^5	3.2×10^5	3.0	2.2×10^4
T7	7.8×10^5	3.4×10^5	2.8	2.8×10^4
T8	7.8×10^5	4.0×10^5	2.2	3.7×10^4
T9	10.0×10^5	3.8×10^5	2.0	2.8×10^4

As an example, Fig. 1 shows a comparison between experimental data of equilibrium isotherm of surface tension for T8 and the calculated theoretical curves. A theoretical dashed curve was calculated using parameters presented in the Table. However, the two stage model according to Eqs. (6)-(9) described the experimental data also rather well using reasonably close values of the parameters. It was shown in the first part, that aggregation starts in adsorbed layer of T8 at the surface pressure around 25 mN/m and higher. Hence, we tried to describe the part of the isotherm in Fig. 1 at $\Pi > 20$ mN/m using an aggregation model. The solid line in Fig. 1 represents results of calculations according to Eqs. (16)-(19) at $\gamma < 50$ mN/m using the following values of parameters: $\omega_1=4\times10^5$ m²/mol, $\Gamma_c=2.45\times10^{-6}$ mol/m², n=1000 and b=4.1×10^4 m³/mol. Note, at n>100 the calculated results do not depend on a number of single surfactant molecules in an aggregate. The beginning of the aggregation process (Π=25 mN/m) is shown by a horizontal line. Fig. 1 shows that at $\gamma < 50$ mN/m both theoretical isotherms (reorientation model and aggregation model) give undistinguished results.

Calculated curves for different adsorption components of T8 are shown in Fig. 2: total adsorption, in states 1 and 2 and in aggregates. Fig. 2 shows that adsorption in the state 2 (with a maximum area per molecule) goes via max value and at the beginning of the aggregation process

Γ_2 is an order of magnitude lower than Γ_1. The latter provides a matching of two theoretical adsorption models in Figure 1. Figure 2 shows that the maximum fraction of the interface covered by aggregates is less than 3-4%. A similar dependency for T9 is shown in Fig. 3. However, in the case of T9 a fraction of the interface covered by aggregates in a saturated layer is a bit higher than in the case of T8: 5-6%.

Comparison of calculations of the total adsorption for T8 according to the model of two states and ellipsometric experimental data are shown in Fig. 4. A dashed line 1 for the total adsorption of T8 is taken from Fig. 2. The latter figure shows that the calculated adsorption based on fitting of equilibrium isotherm of surface tension (Fig. 1) are substantially different from experimental dependency presented in Fig. 4. A possible explanation of the latter observation is as follows. Trisiloxane molecules have probably not less than two kinetically independent trimethylsilyl [-O-Si(CH$_3$)$_3$] groups (see the molecular structure of trisiloxane molecule presented in [1]), which have a possibility to rotate along Si-O bonds. Hence, if we assume that trisiloxane molecule include two kinetically independent trimethylsilyl [-O-Si(CH$_3$)$_3$] groups then equations of state used above (1), (6), (15), and (17) should include a factor 2 in front of RT [29,30]. This means that the fitted values of ω in the Table should be increased by a factor 2. Hence, the total adsorption will be halved after that. Calculated accordingly solid line 2 is shown also in Fig. 4. Note, the latter does not influence the surface tension values, because RT/ω remain the identical value: 2RT/2ω = RT/ω. Note also, a similar situation takes place in the case of ionic 1:1 surfactant molecules (without counter ion excess in the bulk). In that case both charges surfactant molecules and counter ions simultaneously adsorb on the interface [29]. In the case of proteins/polymers the number of independent kinetic units could be in the range of several tens [30].

A dynamic surface tension of T8 at various bulk concentrations in presented in Fig. 5. Note, that experimental dependences do not show a presence of levelling off or an inflection point at Π=22-25 mN/m, that is, in a region where aggregation starts in the adsorbed layer. The latter has previously been observed in other systems [16, 25]. It is possible to assume, that the absence of inflection points on γ vs t dependences for T8 is determined by a relatively low surface concentration of aggregates as deduced from Fig. 2.

For the theoretical description of the experimental dependencies presented in Fig. 5 Eq. (20) was used in combination with Eqs (1)-(5). That is diffusion kinetics of adsorption process was assumed in combination with two state model of adsorption of T8 on the interface. A numerical procedure of solution of those equations has been presented elsewhere [31]. The only unknown parameter in the theory was the diffusion coefficient D. The latter coefficient was found using a

fitting procedure. The dynamic surface tension dependences calculated using that procedure are presented in Fig. 5.

The diffusion coefficients measured by PFG-MNR at low concentrations are D = $(1.89\pm0.05)\cdot10^{-9}$ m^2/s for all surfactants from T9 to T4. The fact that the diffusion coefficients obtained using the fitting procedure (see below) and experimentally determined using PG-NMR agree within their combined errors indicate that in dilute solutions the dynamics is a diffusion controlled process. For more concentrated solutions (above 10^{-3} mol/m) the calculated diffusion coefficients differ considerably from the measured ones at low concentrations by PG-NMR. Below we show the values of diffusion coefficient, D, determined at various bulk concentrations. At low concentrations of T8 solutions (concentrations 0.0035 mmol/l and below) the following value of diffusion coefficient was found: D=(1.0-1.5)$\times10^{-9}$ m^2/s. The latter value of diffusion coefficient was justified using PFG-MNR measurements. Hence, the adsorption mechanism of T8 at low concentrations is solely determined by the diffusion. Note, the surface pressure in this case reaches 25 mN/m only in the end of the adsorption process. That is, the aggregation cannot influence the adsorption process at those bulk concentrations.

At higher bulk concentrations of T8 (0.0158 and 0.158 mmol/l, that is at c<CAC and c≈CAC), the value of the diffusion coefficient was found as D=(3.0-4.0)$\times10^{-10}$ m^2/s. This value is probably lower than the real value of the diffusion coefficient, that shows a presence of a small adsorption barrier. Note, the initial parts of theoretically predicted adsorption curves are located below the experimental data (Fig. 5) which means that the initial stages of adsorption process can only be described using a higher value of the diffusion coefficient. The latter indicated the presence of an adsorption barrier only at the surface pressure Π>10 mN/m, which approximately corresponds to the beginning of the reorientation process of T8 in the adsorbed layer. Why the same does not take place at lower concentrations, where the diffusion coefficient remains constant at this surface pressure? The reason is the rate of the adsorption process, which increases at the bulk concentration increase. If, for example, the rate constant of reorientation process is of the order of 0.1 s^{-1} then for the time scale above 50-100 sec the kinetic mechanism will be replaced by a diffusion one. The latter is the case in Fig. 5.

Dynamic surface tension dependences for T8 at concentration above CAC (0.791 and 1.58 mmol/l) were calculated using numerical calculations of the diffusion equation simulation taking into account an initial adsorption on the interface [32]. The procedure of calculation of diffusion coefficient D was as follows. Using the fitted results of the above experimental dependences at c=CAC the effective diffusion coefficient of monomers D* was determined. After that according to Eq. (21) the diffusion coefficient of monomers D was extracted using the effective diffusion

coefficient D*. The latter procedure results in the following value of the diffusion coefficient of monomers D=(1.5-2.5)×10^{-10} m^2/s, which is almost ten times lower that the real values of the diffusion coefficient of T8 monomers. This may indicate that Joos' model may be too simple to properly account for the contribution of vesicles to the adsorption rate. In any case, it must be recalled that the values of D obtained by PG-NMR correspond to self-diffusion coefficients, which only coincide with the collective diffusion coefficients in the high dilution limit. In general, the collective diffusion coefficients decrease as c is increased due to the interactions between monomers. The interactions between monomers might explain part the small value of D obtained from D*.

Dynamic surface tension dependences for T9 solutions are presented in Fig. 6. Experimental curves have an inflection point at initial stages of adsorption process. The latter is determined by reorientation processes of T9 molecules at the interface. For T9 (as compared with T8) the reorientation process is more distinctively visible because of higher value of ω_2. Note that a similar behaviour was also found for concentrated micellar solutions of other oxyethylene surfactants (Tritons for example [33]). Theoretical dependences at concentrations 0.0314 and 0.13 mmol/l (that is, lower and almost equal to CAC) were calculated according to Eqs (1)-(5) and (20). Extracted diffusion coefficients D (around 10^{-10} m^2/s), also show a possibility of a small potential barrier caused probably by reorientation process. At the bulk concentration of T9 equal to 0.314 mmol/l (that is above CAC) Eq. (21) was additionally used and the following value of the diffusion coefficient was extracted D=5.0×10^{-11} m^2/s, which is fifty times lower than the experimental value of D measured by PG-NMR.

The theoretical dependences of dynamic surface tension for T8 and T9 calculated according to the model, which takes into account the aggregation of molecules on the interface (Eqs (17)-(20)) in the region Π>20 mN/m, almost coincide with the calculations according to the two state model if we used identical values of diffusion coefficients.

Conclusions

A theoretical analysis of the experimental data [1] on equilibrium and dynamic interfacial tension of trisiloxanes with various number of oxyethylene groups is presented. The important feature of aqueous solutions of T6, T7, T8 and T9 is a formation of two dimensional aggregates in adsorbed layer. The presence of inflections points on dependences of dynamic interfacial tension on time for T9 aqueous solutions was also detected[1]. It is shown in this paper that experimental results on equilibrium and dynamic interfacial tension agree well with combined theoretical model, which is based on earlier developed two stage and aggregation models. According to the

two stage model there are two states of trisiloxane molecules on the surface layer. Molecules in those two states occupy different surface area. According to the second aggregation model, adjusted for trisiloxane molecules, molecules occupying the lowest area on the interface can form two dimensional aggregates. It was assumed that trisiloxanes molecules have two kinetically independent trimethylsilyl [-O-Si(CH$_3$)$_3$] groups (see the molecular structure of trisiloxane molecule presented in[1]). The latter have a possibility to rotate along Si-O bonds and, hence, trisiloxane molecule includes two kinetically independent trimethylsilyl [-O-Si(CH$_3$)$_3$] groups. The latter assumption allowed us to agree the theoretical model and experimental data on ellipsometric measurement of adsorption.

Acknowledgement

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Figure legends

Fig. 1. Experimental isotherm of equilibrium surface tension for T8 (points). The dashed theoretical curve calculated according to the model of two states using the value of parameters presented in the Table. The solid curve calculated according to the aggregation model. The horizontal line corresponds to the beginning of the aggregation according to [1].

Fig. 2. Adsorption of T8 on bulk concentration of surfactant calculated according to the two states model. Curve 1 is a total adsorption, curve 2 is adsorption in the state 1 (single molecules), curve 3 is adsorption in the state 2; curve 4 is adsorption of clusters.

Fig. 3. The same as in Figure 2 but for T9 solutions.

Fig. 4. Dependency of adsorption of T8 molecules on the bulk concentration. Points are experimental data (ellipsometry), a dashed line 1 - calculated total adsorption according to Figure. 2, solid line 2 - calculated using twice higher value of ω (see the text).

Fig. 5. Dynamic surface tension of T8 solutions at different bulk concentrations. Points are experimental data. Theoretical curves are calculated using the two-state model.
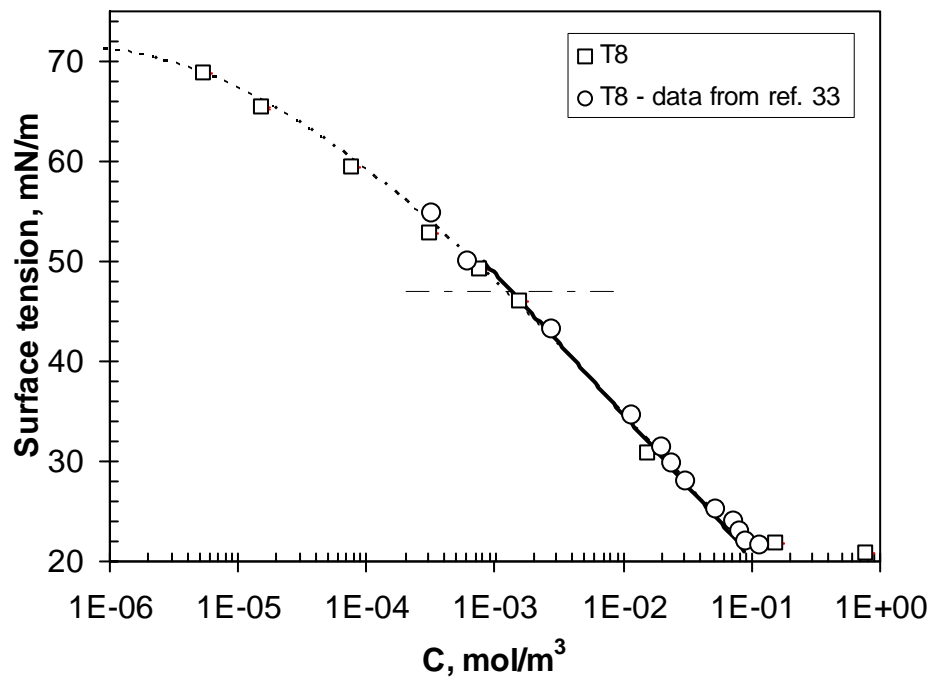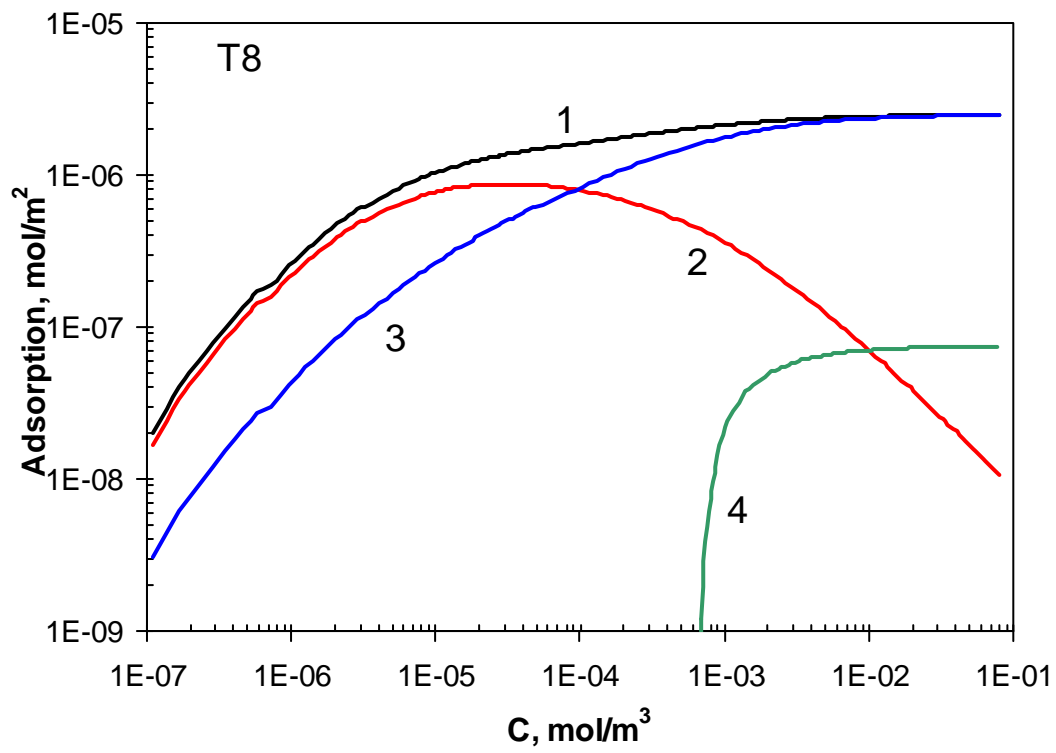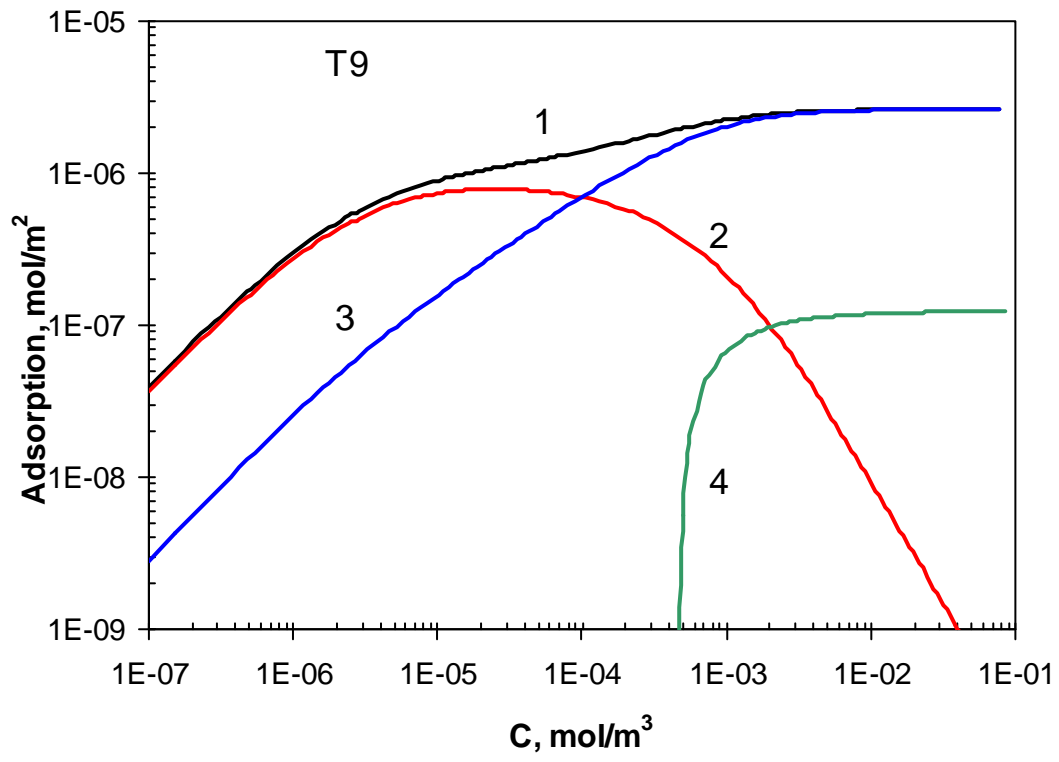
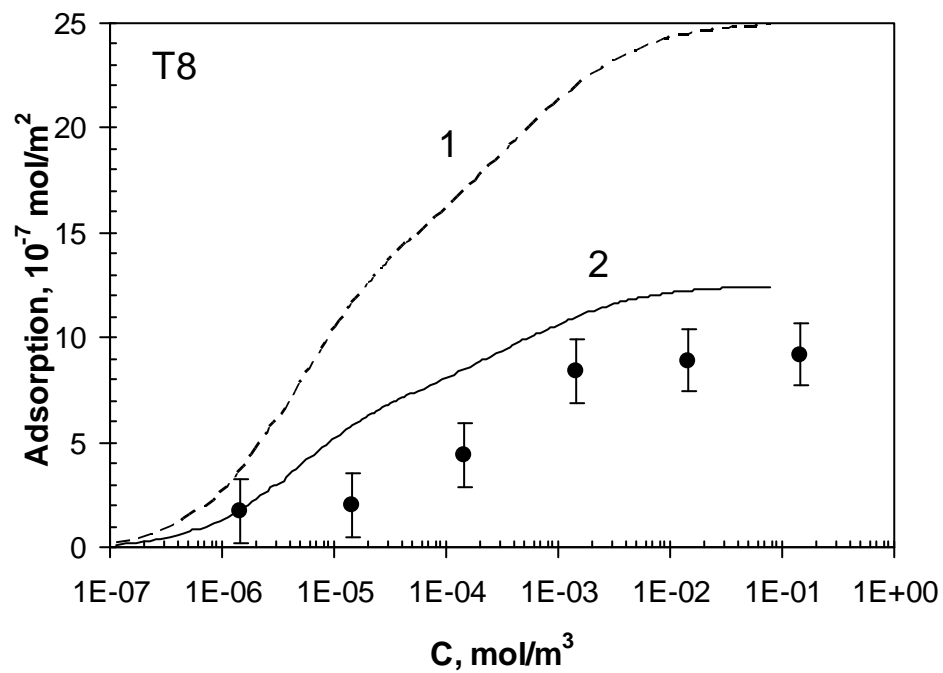**Fig. 6**. The same as in the Figure 5 but for T9 solutions.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5.

Fig. 6.