Activity coefficient at infinite dilution of aqueous solutions of nonionic hydrocarbon and fluorocarbon surfactants as well as their ternary mixtures

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Activity coefficients at infinite dilution of the aqueous solutions of nonionic hydrocarbon surfactants, p-(1,1,3,3-tetramethylbutyl) phenoxypoly(ethylene glycols), Triton X-100 (TX100) and Triton X-165 (TX165), fluorocarbon surfactants, Zonyl FSN-100 (FSN100) and Zonyl FSO-100 (FSO100) and their ternary mixtures were determined from the Gracia-Fadrique et al. method for non-volatile compounds. The values of activity coefficients were calculated taking into account the surface tension data of the studied systems at 293K and compared to those determined on the basis of the values of the contact angle of solutions on the polytetrafluoroethylene (PTFE) and polymethyl methacrylate (PMMA) surfaces and the solid-liquid interface tension.

1. INTRODUCTION

In the literature there has been an increasing effort to study the relationship between the properties of the vapour-liquid interface and the activity of a solute in the bulk liquid solution. This effort is motivated, among other things, by the aim to determine values of activity
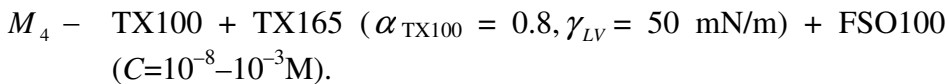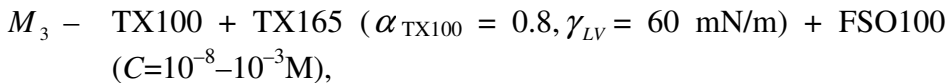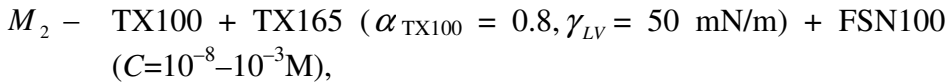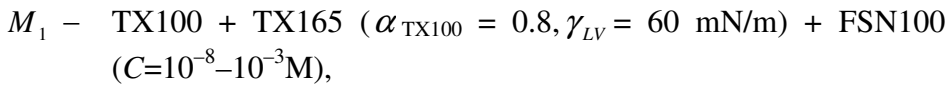
coefficients from the surface tension data for the systems where classical methods of their determination cannot be used. The studies are focused, especially, on very dilute solutions, because limiting activity coefficients are of great practical importance in separation technology, environmental pollution control, chemical technology, food technology, and biotechnology applications as well as of theoretical interest (for example, in solution chemistry and biothermodynamics). The determination of activity coefficients by the traditional methods based on the liquid–vapour equilibrium does not consider the group of non-volatile substances such as proteins, polymers and surfactants.

The most common methods for measuring infinite dilution activity coefficient data are Gas–Liquid Chromatography (GLC), static methods, ebulliometric and dilutor techniques [1-3]. Gracia-Fadrique and his group have developed a method for determining the activity coefficients of non-volatile compounds [4-6]. Their method is based on the equilibrium condition between the surface and bulk phases rather than that between the vapour and liquid or liquid and liquid phases. They have used the Volmer surface equation of state and the Gibbs adsorption equation to derive an expression for the surface chemical potential. Using this approach, they have determined the activity coefficient of some amphiphiles at infinite dilution [4-6].

Among surfactants, fluorocarbon ones have many exceptional chemical and physical properties, which cannot be found in their conventional hydrocarbon counterparts. They have impressed ability to decrease the interfacial tension and it is exploited to be coatings, emulsions, cleaners, foams, and oil-fire extinguishing agents [7, 8]. They usually mix with hydrocarbon surfactants in applications. Fluorocarbon/hydrocarbon mixtures often exhibit nontrivial phase behaviour that originates from the nonideal mixing of alkanes and perfluoroalkanes. The earlier studies showed that the nonionic fluorocarbon surfactants, Zonyl FSN-100 (FSN100) and Zonyl FSO-100 (FSO100) at 293K have better efficiency and effectiveness in the reduction of surface tension of water than hydrocarbon p-(1,1,3,3-tetramethylbutyl)phenoxypoly(ethylene glycols), Triton X-100 (TX100) and Triton X-165 (TX165) [9]. It was also found that for FSN100 and FSO100 depending on the physicochemical parameters used for critical micelle concentration (*CMC*) determination, it is possible to obtain its two different values corresponding to different sizes of the micelles [10], which is difficult to come across in the literature. On the other hand, in the range of FSN100 and FSO100 concentrations in solution in which

they are present in the monomeric form, contrary to Tritons, they are weak wetting agents [11]. Also when these fluorocarbon surfactants were added to the binary mixture of TX100+TX165 at the monomer mole fraction of TX100 in the bulk phase equal to 0.8, that is the mixture with the largest synergetic effect in the reduction of surface tension of water among those for α = 0.2, 0.4, 0.6 and 0.8, the values of the contact angle of such ternary mixtures on the polytetrafluoroethylene (PTFE) surface were smaller than the appropriate θ for single FSN100 or FSO100, but were much higher than those of hydrocarbon surfactants and their binary mixture [11]. From this point of view, it was interesting to calculate the infinite dilution activity coefficient of TX100, TX165, FSN100 and FSO100 as well as their ternary mixtures on the basis of the values not only of their surface tension but also contact angle on polymeric solids, polytetrafluoroethylene (PTFE) and polymethyl methacrylate (PMMA) . For this purpose the surface tension values of the aqueous solution of the mentioned surfactants and their mixtures as well as contact angle on the PTFE and PMMA surfaces from Ref. [11] and [12] were used here.
The following ternary mixtures of surfactants were studied:

M_1 – TX100 + TX165 (α_{TX100} = 0.8, γ_{LV} = 60 mN/m) + FSN100 (C=10^{-8}–10^{-3}M),

M_2 – TX100 + TX165 (α_{TX100} = 0.8, γ_{LV} = 50 mN/m) + FSN100 (C=10^{-8}–10^{-3}M),

M_3 – TX100 + TX165 (α_{TX100} = 0.8, γ_{LV} = 60 mN/m) + FSO100 (C=10^{-8}–10^{-3}M),

M_4 – TX100 + TX165 (α_{TX100} = 0.8, γ_{LV} = 50 mN/m) + FSO100 (C=10^{-8}–10^{-3}M).

Thus, for example, the mixture M_1 was prepared by adding FSN100 at different concentrations to the binary mixture of TX100+TX165, where the monomer mole fraction of TX100, α, was equal to 0.8, at γ_{LV} of the binary mixture equal to 60 mN/m. The binary mixture at the concentrations at which γ_{LV} = 60 and 50mN/m were chosen in the experiments because at these values of γ_{LV} the calculations of mole fraction of surfactants as well as intermolecular interaction parameters at the water-air interface have been performed [13].

2. THEORY

Using the experimental surface tension data Gracia-Fadrique et al. [4-6] calculated the infinite dilution activity coefficient (γ^∞) of the surfactants. This method combines the first natural nonideal surface equation of state of the Vander Waals type, the Volmer equation ($\pi(A - A_0) = RT$), and the Gibbs adsorption equation and is based on the application of equilibrium conditions between the bulk and surface phases. The main equation of the model can be written as:

$$\ln\left(\frac{\pi^*}{x}\right) = \frac{\pi_m A_0}{RT}\left(1 - \pi^*\right) + \ln \gamma_{LV}^\infty \tag{1}$$

where $\pi^* = \pi / \pi_m$ is the reduced surface pressure, $\pi = \gamma_{LV}^0 - \gamma_{LV}$ is the surface pressure, i.e. the difference between the surface tension of pure solvent (γ_{LV}^0) and that of the solution (γ_{LV}), $\pi_m = \pi_{CMC}$ is the maximum surface pressure, and A_0 is a constant of the Van der Waals type. Equation (1) is only valid in the interval $0 < x < x_{CMC}$, where x is the concentration. The γ_{LV}^∞ parameter can be obtained from the linear fit of Eq.(1) to high quality experimental data.

In the presented studies the values of γ^∞ for the TX100, TX165, FSN100 and FSO100 were calculated not only on the basis of the values of surface tension (γ_{LV}) but also those of the contact angle (θ) of their solutions on the PTFE and PMMA surfaces. For the studied ternary mixtures of surfactants, the values of γ^∞ were also calculated from those of the solid-liquid interface tension (γ_{SL}). It was possible because of the linear behaviour of the $\ln(\pi^* / x) = f(1 - \pi^*)$ curves in the premicellar region for different π i.e. the difference between the surface tension/contact angle/solid-liquid interface tension of the solvent and that of the solution (Figs. 1-5).

According to the Young equation [14] :

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta \tag{2}$$

the contact angle (θ) depends on the surface tension of solid (γ_{SV}) and liquid (γ_{LV}) as well as the solid-liquid interface tension (γ_{SL}). These

parameters directly depend on the adsorption of the surfactants at the solid-air, liquid-air and solid-liquid interfaces and indirectly on their behaviour in the bulk phase. The main problems of using the Young equation is in expressing the interfacial solid–liquid tension as a function of surface tension of a solid and a liquid.

There are two basic approaches to this problem. The first is based on the assumption that the surface tension of a solid and a liquid can be divided into parts resulting from different kinds of intermolecular interactions and the solid-liquid interface tension is a function of these parts of surface tension of a solid and a liquid [15-17]. The second assumes that the solid-liquid interface tension is a function of the total surface tension of a solid and a liquid. Van Oss et al. [16, 17] represent the first approach to the problem of solid-liquid interface tension in the Young equation, which is the most commonly used for determination of the surface tension of different kinds of solids. In turn, Neumann et al. [18-20] who represent the latter point of view to the solid-liquid interface tension, analyzing the contact angles of different liquids on the polymers measured by Zisman et al. [21, 22] showed that there is the linear dependence between the parameter of the interface interaction and the polymer-liquid interface tension. Based on this they proposed the equation of state which was modified by them [18-20].

To show the influence of the coverage with a layer of studied mixed surfactants on the surface properties of PTFE and PMMA, the surface tension of the pristine surfaces was analyzed by using the van Oss et al. [16, 17] and Neumann et al. [18-20] approaches to the solid- liquid interface tension [23]. For this purpose the contact angles of apolar and polar liquids on the PTFE and PMMA surfaces were used [24, 25].
In the presented studies the values of γ_{SL} were calculated taking into account the literature data of the surface tension and contact angle of the studied mixtures on the PTFE and PMMA surfaces [11] in three ways. The first one, denoted as γ_{SL}^1, and calculated on the assumption that γ_{SV} is constant and equal to 20.24 and 39.21 mN/m for PTFE and PMMA, respectively [25, 26]. The second way, denoted as γ_{SL}^2, is evaluated from the values of γ_{SV} calculated on the basis of the van Oss equation, and the third one, called γ_{SL}^3 on the basis of the values of γ_{SV} calculated from the Neumann equation and clean surfaces. Next these values were used for γ^∞ calculations for PTFE but in two different ways that is the first in

comparison to water (γ^∞ for $\pi = \gamma^0 - \gamma$), and the second to the binary mixture of surfactants (γ_M^∞ for $\pi = \gamma_M^0 - \gamma$) to which the third surfactant was added. These values were compared to those calculated on the basis of the values of the contact angle, θ, for $\pi = \theta^0 - \theta$ (θ^0 is the contact angle for water) and $\pi = \theta^M - \theta$ $\pi = \theta^0 - \theta$ (θ^M is the contact angle for binary mixture of surfactants). For PMMA it was possible to calculate the values of γ^∞ only on the basis of the values of γ_{SL} calculated from the Neumann et al. equation.

3.   RESULTS AND DISCUSSION

The values of the logarithm of the infinite dilution activity coefficient for TX100, TX165, FSN100 and FSO100 calculated from those of their surface tension (γ_{LV}^∞), contact angle on PTFE ($\gamma_{\theta,PTFE}^\infty$) and PMMA ($\gamma_{\theta,PMMA}^\infty$) surfaces (Table 1) and $\ln(\pi^*/x) = f(1 - \pi^*)$ curves (Figs. 1 and 2) clearly indicate that for the studied fluorocarbon surfactants the values of $\ln\gamma_{LV}^\infty$ are larger than those for TX100 and TX165. The situation is quite different if the values of $\ln\gamma_{\theta,PTFE}^\infty$ and $\ln\gamma_{\theta,PMMA}^\infty$ are taken into account which confirm the earlier conclusions that FSN100 and FSO100, contrary to Tritons, are weak wetting agents [11].

Table 1. The values of the logarithm of the infinite dilution activity coefficient for TX100, TX165, FSN100 and FSO100 calculated on the basis of the values of their surface tension (γ_{LV}^∞), contact angle on PTFE ($\gamma_{\theta,PTFE}^\infty$) and PMMA ($\gamma_{\theta,PMMA}^\infty$) surfaces.

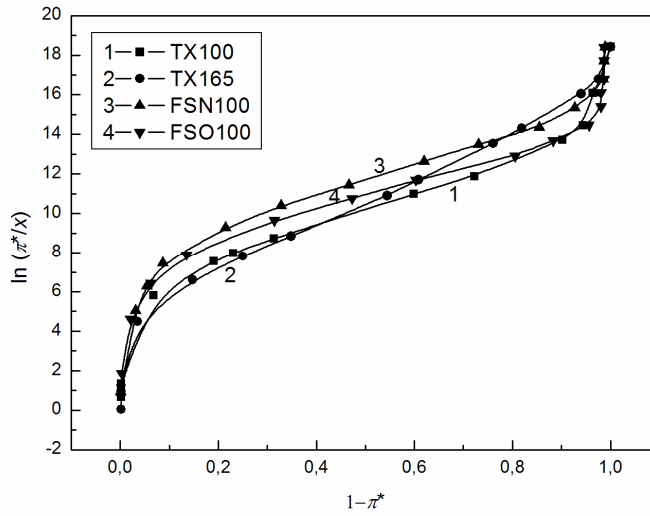|	TX100	TX165	FSN100	FSO100
$\ln\gamma_{LV}^\infty$	6.104	4.909	7.727	7.141
$\ln\gamma_{\theta,PTFE}^\infty$	5.296	4.642	4.664	4.633
$\ln\gamma_{\theta,PMMA}^\infty$	5.325	4.600	4.752	4.462

Fig. 1. A plot of the values of $\ln(\pi^*/x)$ of the aqueous solutions of nonionic surfactants TX100 (curve 1), TX165 (curve 2), FSN100 (curve 3) and FSO100 (curve 4) calculated on the basis of the values of the surface tension vs. the $(1-\pi^*)$.
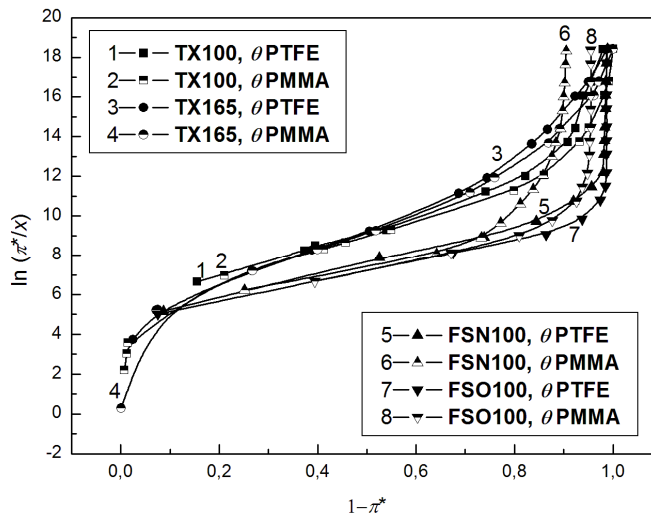

Fig. 2. A plot of the values of $\ln(\pi^*/x)$ of the aqueous solutions of nonionic surfactants TX100 (curves 1 and 2), TX165 (curves 3 and 4), FSN100 (curve 5 and 6) and FSO100 (curves 7 and 8) calculated on the basis of the values of the contact angle on the PTFE (curves 1,3,5 and 7) and PMMA (curves 2,4,6 and 8) surfaces vs. the $(1-\pi^*)$.

The value of $\ln \gamma_{LV}^{\infty}$ for TX165 is smaller than for TX100, which according to the literature [27], is attributed to the hydrophilic nature of ethylene oxide (EO), the larger number of EO units in the surfactant molecule, the smaller the tendency to migrate to the surface and to form micelles. Thus, the critical micelle concentration increases for TX165, and correspondingly the activity coefficients at infinite dilution decrease, as these values mark the surface activity, that is, the tendency of getting adsorbed at the interface of these substances. Both Zonyls, FSN100 and FSO100, are also ethoxylated nonionic fluorosurfactants, having respectively an average 14 (from 1 to 26) and 10 (from 1 to 16) oxyethylene units in their molecules [11]. The values of $\ln \gamma_{LV}^{\infty}$ for FSN100 are larger than for FSO100 which confirms the main role of the fluorocarbon chains in the adsorption and micellization processes.

Table 2. The values of the logarithm of the infinite dilution activity coefficient of the aqueous solutions of ternary mixtures of surfactants $(M_1 - M_4)$ calculated on the basis of the values of the surface tension ($\ln \gamma_{LV}^{\infty}$, $\ln \gamma_{LV,M}^{\infty}$), contact angle on the PTFE ($\ln \gamma_{\theta,PTFE}^{\infty}$, $\ln \gamma_{\theta,PTFE,M}^{\infty}$) and PMMA ($\ln \gamma_{\theta,PMMA}^{\infty}$, $\ln \gamma_{\theta,PMMA,M}^{\infty}$) surfaces in comparison to water ($\ln \gamma_{LV}^{\infty}$, $\ln \gamma_{\theta,PTFE}^{\infty}$, $\ln \gamma_{\theta,PMMA}^{\infty}$) and to the binary mixture of surfactants to which the third surfactant was added ($\ln \gamma_{LV,M}^{\infty}$, $\ln \gamma_{\theta,PTFE,M}^{\infty}$, $\ln \gamma_{\theta,PMMA,M}^{\infty}$).

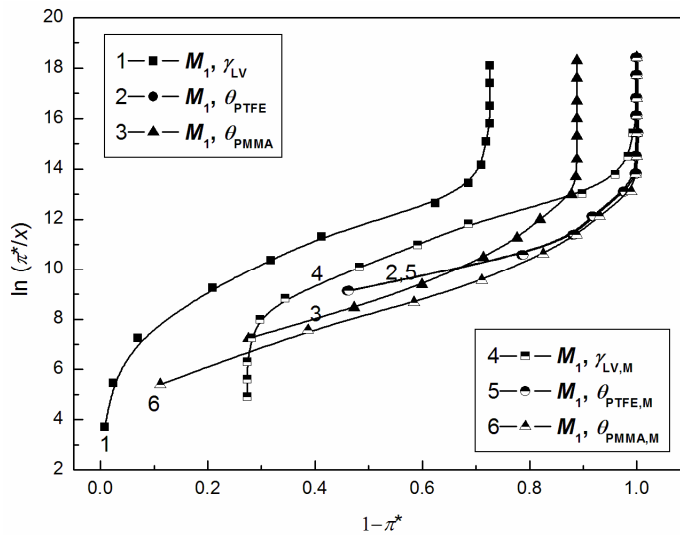|	M_1	M_2	M_3	M_4
$\ln \gamma_{LV}^{\infty}$	7.667	7.303	7.231	7.213
$\ln \gamma_{\theta,PTFE}^{\infty}$	6.723	5.612	5.957	5.815
$\ln \gamma_{\theta,PMMA}^{\infty}$	5.114	4.149	5.228	5.635
$\ln \gamma_{LV,M}^{\infty}$	6.820	5.687	6.260	5.432
$\ln \gamma_{\theta,PTFE,M}^{\infty}$	6.715	5.607	6.258	5.373
$\ln \gamma_{\theta,PMMA,M}^{\infty}$	5.301	4.875	4.785	4.722

Fig. 3. A plot of the values of $\ln(\pi^*/x)$ of the aqueous solutions of ternary mixture of surfactants, M_1, calculated on the basis of the values of the surface tension (curves 1 and 3), contact angle on the PTFE (curves 2 and 5) and PMMA (curves 3 and 6) surfaces in comparison to water (curves 1-3) and to the binary mixture of surfactants to which the third surfactant was added (curves 4-6) vs. the $(1 - \pi^*)$.

This may be also connected with the change of water structure in the presence of surfactants. In the literature it can be found that the oxyethylene group can be associated with two molecules of water [28] or that most of water molecules are mechanically trapped in the polyoxyethylene chains of nonionic surfactants, with 5.2 to 10.5 water molecules per oxyethylene unit [29, 30]. It is also noted that different water species of varying strength and coordination participate in the hydration of the EO groups and a significant portion of the water molecules present in the headgroup region with a preferred orientation was found to be forming weak hydrogen bonds in a liquidlike state [31] and that there is a gradual change in the hydration of the oxyethylene groups along the chain [32]. Tadros claimed that the fluorocarbon chain has a higher water structure promoting ability than that of the hydrocarbon chain [33]. Hence the hydrogen bonded water structure around the fluorocarbon chains is more extensive and micellization requires breaking more water structure around the fluorocarbon surfactant chain than the corresponding hydrocarbon chain [7, 8].

The values of $\ln \gamma_{LV}^{\infty}$ for the studied ternary mixtures of surfactants, M_1, M_2, M_3 and M_4, (Table 2, Fig. 3 as an example) are larger than appropriate $\ln \gamma_{\theta,PTFE}^{\infty}$ and $\ln \gamma_{\theta,PMMA}^{\infty}$, independently of the way of π calculations.

Table 3. The values of the logarithm of the infinite dilution activity coefficient of the aqueous solutions of ternary mixtures of surfactants ($M_1 - M_4$) calculated on the basis of the values of γ^1_{SL}, γ^2_{SL} and γ^3_{SL} for PTFE surface in comparison to water ($\ln \gamma_{\gamma_{SL}(1),PTFE}^{\infty}$, $\ln \gamma_{\gamma_{SL}(2),PTFE}^{\infty}$, $\ln \gamma_{\gamma_{SL}(3),PTFE}^{\infty}$) and to the binary mixture of surfactants to which the third surfactant was added ($\ln \gamma_{\gamma_{SL}(1),PTFE,M}^{\infty}$, $\ln \gamma_{\gamma_{SL}(2),PTFE,M}^{\infty}$, $\ln \gamma_{\gamma_{SL}(3),PTFE,M}^{\infty}$).

	M_1	M_2	M_3	M_4
$\ln \gamma_{\gamma_{SL}(1),PTFE}^{\infty}$	5.532	5.254	6.080	6.201
$\ln \gamma_{\gamma_{SL}(2),PTFE}^{\infty}$	6.146	6.792	6.304	7.640
$\ln \gamma_{\gamma_{SL}(3),PTFE}^{\infty}$	6.466	4.332	5.942	6.586
$\ln \gamma_{\gamma_{SL}(1),PTFE,M}^{\infty}$	5.645	5.497	6.241	6.455
$\ln \gamma_{\gamma_{SL}(2),PTFE,M}^{\infty}$	6.223	7.101	6.411	7.914
$\ln \gamma_{\gamma_{SL}(3),PTFE,M}^{\infty}$	6.836	7.590	7.079	7.172

In the case of PTFE there are also differences in the values of the logarithm of the infinite dilution activity coefficient calculated on the basis of the values of the solid-liquid interface tension (γ_{SL}) on the assumption that $\gamma_{SV} = $ const and $\gamma_{SV} \neq$ const (Table 3, Fig. 4 as an example).

The values of $\ln \gamma^{\infty}$ calculated for the studied mixtures frome those of γ_{SL}^3 for PMMA are much larger than those calculated the appropriate contact angle ones (Table 4, Fig. 5). It is interesting that both the values of $\ln \gamma_{\theta,PMMA}^{\infty} / \ln \gamma_{\gamma_{SL}(3),PMMA}^{\infty}$ and $\ln \gamma_{\theta,PMMA}^{\infty} / \ln \gamma_{\gamma_{SL}(3),PMMA,M}^{\infty}$ are very similar for all studied mixtures.
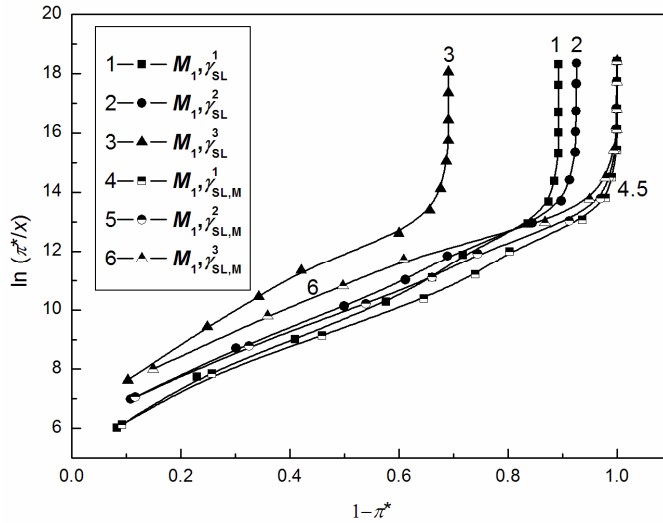
Fig. 4. A plot of the values of $\ln(\pi^*/x)$ of the aqueous solutions of ternary mixture of surfactants, M_1, calculated on the basis of the values of γ^1_{SL} (curves 1 and 3), γ^2_{SL} (curves 2 and 5) and γ^3_{SL} (curves 3 and 6) for the PTFE surface in comparison to water (curves 1-3) and to the binary mixture of surfactants to which the third surfactant was added (curves 4-6) vs. the $(1 - \pi^*)$.
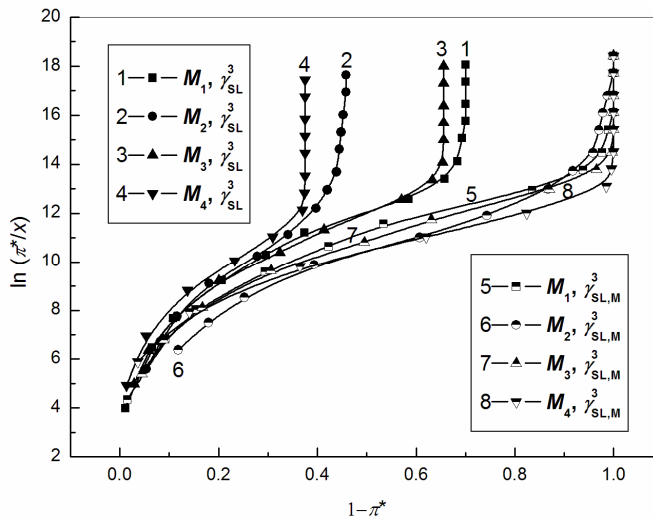

Fig. 5. A plot of the values of $\ln(\pi^*/x)$ of the aqueous solutions of ternary mixtures of surfactants, M_1 (curves 1 and 5), M_2 (curves 2 and 6), M_3 (curves 3 and 7) and M_4 (curves 4 and 8) calculated on the basis of the values of γ^3_{SL} in comparison to water (curves 1-4) and to the binary mixture of surfactants to which the third surfactant was added (curves 5-8) vs. the $(1 - \pi^*)$.

Table 4. The values of the logarithm of the infinite dilution activity coefficient of the aqueous solutions of ternary mixtures of surfactants ($M_1 - M_4$) calculated on the basis of the values of γ^3_{SL} in comparison to water ($\ln \gamma^\infty_{\gamma_{SL}(3),PMMA}$) and to the binary mixture of surfactants to which the third surfactant was added ($\ln \gamma^\infty_{\gamma_{SL}(3),PMMA,M}$).

	M_1	M_2	M_3	M_4
$\ln \gamma^\infty_{\gamma_{SL}(3),PMMA}$	8.810	7.030	8.054	8.902
$\ln \gamma^\infty_{\gamma_{SL}(3),PMMA,M}$	8.955	7.810	7.639	8.063

4. CONCLUSIONS

There were found the linear relationships between $\ln(\pi^*/x)$ and $(1-\pi^*)$ in the premicellar region for aqueous solutions of studied nonionic surfactants (TX100, TX165, FSN100 and FSO100) and their ternary mixtures (M_1-M_4). Calculated on the basis of these dependences and different values of π, the values of the infinite dilution activity coefficients are different and confirm better activity of the systems including fluorocarbon surfactants at the water-air interface. To correlate the values of this activity coefficient calculated in different ways, other calculations and measurements should be performed and different models should be used in calculations.

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Katarzyna Szymczyk studied chemistry at the Maria Curie-Skłodowska University in Lublin, Poland from 1997-2002. Then she was employed at the Department of Interfacial Phenomena, Faculty of Chemistry UMCS in Lublin. In 2007 she received her Ph.D. degree in chemistry. She has published over 45 original papers in professional journals and books. Her research areas are interfacial phenomena at the solid-liquid, solid-gas and liquid-liquid inter-faces, adsorption, wettability, adhesion and surface and volumetric properties of hydrocarbon and fluorocarbon surfactants as well as their multicomponent mixtures.

Anna Taraba is a student working at the Depart-ment of Interfacial Phenomena (Faculty of Che-mistry of Maria Curie-Skłodowska University in Lublin, Poland) as a candidate for doctor's degree. Her scientific interest is largely concen-trated on the interactions between different kinds of surfactants and their mixtures with the phenolic compounds at the water-air and solid-water interfaces. She published two papers in prestigious journals and presented three posters at national conferences.