# Adsorption of Diastereomerically Pure Sodium *cis-* and *trans-*(2-*n*-Alkyl-1,3-dioxan-5-yl) Sulfates at the *n*-Heptane−Water Interface[†]

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A systematic study concerning adsorption and aggregation of chemodegradable, diastereomerically pure sodium *cis-* and *trans-*(2-*n*-alkyl-1,3-dioxan-5-yl) sulfates (alkyl: *n*-C$_9$H$_{19}$ and *n*-C$_{11}$H$_{23}$) in the system consisting of *n*-heptane in contact with aqueous 0.2 M NaCl at 31 °C has been undertaken. The role of the six-membered 1,3-dioxane ring has been discussed in terms of comparison between studied surfactants and "classical" sodium decyl and dodecyl sulfates. Surface parameters of compounds under study at the oil−water interface, i.e., surface tension reduction ($\pi$), surface excess concentration ($\Gamma$), surface area demand per molecule ($A$), critical micelle concentration (cmc), standard free energy of adsorption ($\Delta G^{o}_{ads}$), and of micellization ($\Delta G^{o}_{cmc}$), show differences due to the alkyl chain length and to the hydrophilic, i.e., sulfate group configuration at the C-5 atom of the 1,3-dioxane ring. The cmc, $\Delta G^{o}_{ads}$, and $\Delta G^{o}_{cmc}$ values are lower for the *trans* isomers than for the *cis* ones, whereas the effectiveness of surface tension reduction is nearly the same for both isomers. Additionally, the interfacial tensions of the studied acetal-type isomers have been described for the heptane− aqueous NaCl systems containing Aerosol OT. According to our findings the configuration of the − OSO$_3$- Na polar group at the C-5 carbon atom of the 1,3-dioxane ring, i.e., equatorial in *trans* isomers and axial in *cis* isomers, involves diastereomeric differentiation in the aggregation abilities.

## Introduction

The behavior of interfaces between the oil and aqueous phases is of crucial importance in a wide variety of industrial areas involving surfactants, detergent and lubricating systems, in many agrochemical, pharmaceutical, and food preparations, as well as in a number of processes encountered in the oil industry.

The oil−water interfacial tension in systems containing an anionic surfactant (Aerosol OT or sodium dodecyl sulfate, SDS) at the aggregation point can be made to pass through an ultralow minimum, $\gamma_{c,min}$, by adjustment of the salt concentration or the concentration of a long-chain alcohol (acting as a cosurfactant). For the twin-tailed surfactant (AOT) the $\gamma_{c,min}$ value can be attained in the absence of the cosurfactant, whereas the presence of the latter is necessary in the case of the single-tailed SDS.[1,2] Additionally, in the heptane−aqueous NaCl system containing mixtures of AOT and SDS (in the absence of cosurfactant), the steady increase in SDS concentration resulted in the water-in-oil droplets growth in size until the system has been inverted to the oil-in-water-type aggregates.[1d] Ninham et al.[3] and Mukherjee et al.[4] have established an interesting "geometric" approach to explain the way in which monolayers tend to curve and the Winsor transitions occur. Accordingly, the minimum tension is achieved when the effective cross sectional area, $a_h$, of the hydrophilic group exceeds $a_c$ of the hydrophobic chain. Under conditions where $a_h > a_c$ two-phase systems consisting of an oil-in-water (o/w) microemulsion in equilibrium with an excess of oil can appear. Water-in-oil (w/o) microemulsions in

equilibrium with an excess of the aqueous phase can be formed at higher salt concentrations ($a_h < a_c$). The droplet size in the mentioned two-phase systems remains in straight relation with the "natural", spontaneous curvature, $H_o$, favored by the surfactant (or surfactant mixture) film formed at the oil−water interface.[5]

The present work introduces a further reasoning to the above idea. Its main purpose was to describe quantitatively the way in which the packing of two surfactants, namely twin-tailed AOT and single-tailed sodium *cis-* or *trans-*(2-*n*-alkyl-1,3-dioxan-yl) sulfates[6] (cis-C$_n$ and trans-C$_n$ in Figure 1) or sodium alkyl sulfates (C$_n$OSO$_3$Na), affects the interfacial tensions $\gamma_c$ in mixed adsorbed films. The application of anionics other than SDS, especially those differing in geometrical structure,[6] could increase variety and effectivity of thermodynamically stable Winsor II−Winsor III−Winsor I system transitions. We have chosen the diastereomerically pure disubstituted 1,3-dioxane derivatives (representing chemodegradable surfactants[6]) because their self-assembling abilities at the air−water interface are different.[6a,b] The adsorption of such pure, diastereomeric entities at the oil−water boundary has not been described in the literature yet. By combination of two different surfactants, we show here that interfacial tensions can be distinguished by the sulfate group configuration at the 1,3-dioxane ring. Furthermore, we discuss in detail the influence of alkyl chain length and six-membered ring of the studied diastereomeric surfactants upon their adsorption and aggregation parameters in the alkane− aqueous NaCl systems in comparison with the same systems containing sodium *n*-decyl and *n*-dodecyl sulfates.

## Experimental Section

**Materials.** The synthesis and properties of pure sodium *cis-* and *trans-*(2-*n*-alkyl-1,3-dioxolan-5-yl) sulfates (hereafter called

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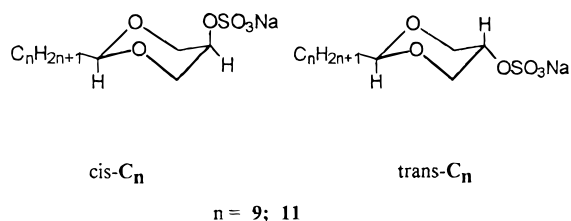*J. Phys. Chem. B, Vol. 103, No. 26, 1999* **5513**



n = 9; 11

**Figure 1.** Single-tailed sodium *cis*- and *trans*-(2-*n*-alkyl-1.3-dioxan-yl) sulfates (cis-$C_n$ and trans-$C_n$).
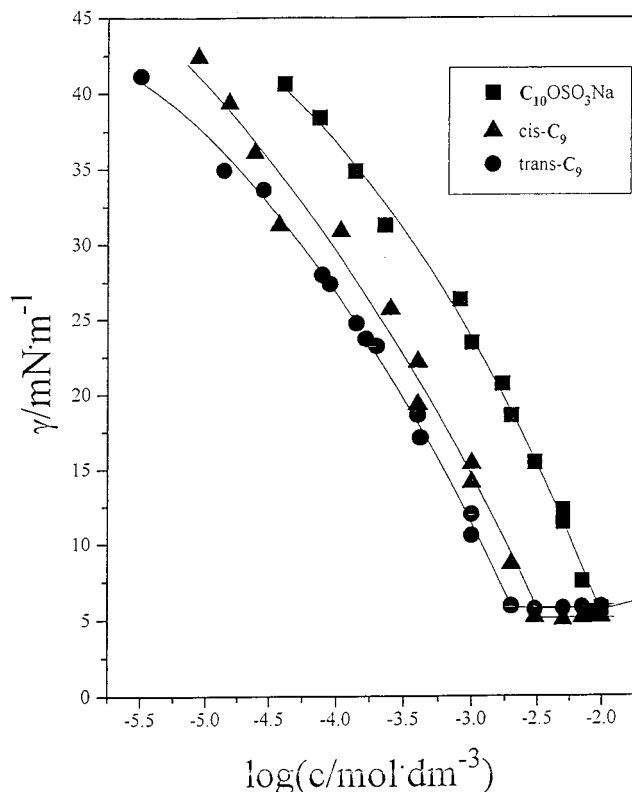


**Figure 2.** Equilibrium interface tension-concentration (log $c$) isotherms of sodium cis- and *trans*-(2-*n*-nonyl-1.3-dioxan-yl) sulfates: *cis*-$C_9$, *trans*-$C_9$, and sodium *n*-decyl sulfate ($C_{10}OSO_3Na$) in 0.2 M NaCl at 31 °C.
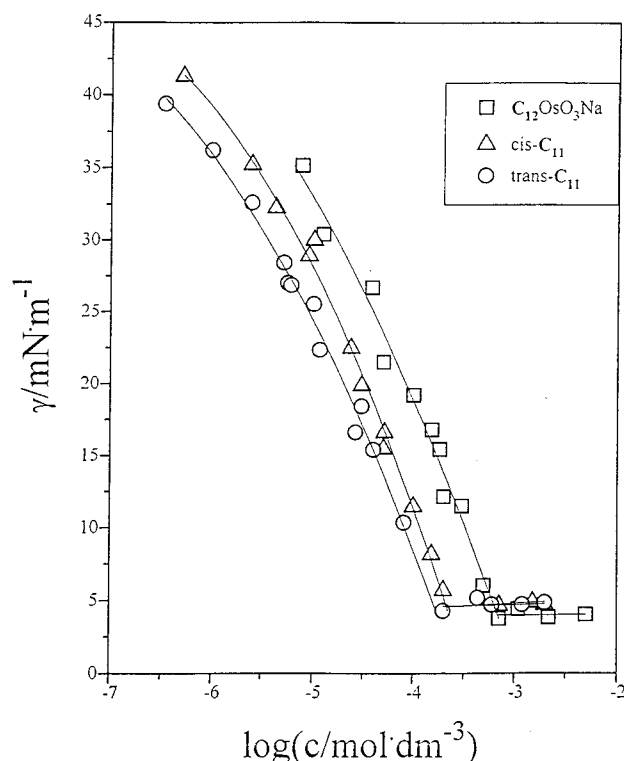


**Figure 3.** Equilibrium interface tension-concentration (log c) isotherms of sodium *cis*- and *trans*-(2-n-undecyl-1.3-dioxan-yl) sulfates: cis-$C_{11}$, *trans*-$C_{11}$, and sodium *n*-dodecyl sulfate ($C_{12}OSO_3Na$) in 0.2 M NaCl at 31 °C.

Tensions below 18 mN m$^{-1}$ were determined using a Krûss spinning-drop tensiometer SITE 04. Sets of measurements were taken at intervals until no significant change in tension occurred. The accuracy of experimental data of the $\gamma$ vs c isotherms for the studied compounds remains ±0.3 mN m$^{-1}$.

### Results and Discussion

In the present work, we investigated the effect of changes in geometric structure of surfactant on the oil−water interfacial tension. We carried out two kinds of experiments. In one case, the interfacial tension, $\gamma$ was obtained as a function of diastereomeric surfactant (cis-$C_9$, trans-$C_9$, and cis-$C_{11}$, trans-$C_{11}$) concentration, c, at constant salt concentration, $m_s$, in the *n*-heptane−water system. In the second set of experiments we took AOT at a fixed concentration, $m_{AOT}$, close to and above its cmc in the system containing heptane and aqueous NaCl and progressively increased the chemodegradable surfactant concentration, $m_1$. We also did two experiments for $C_{10}OSO_3$-Na and $C_{12}OSO_3Na$ to compare surface activity of the acetal-type surfactants and the straight chain "classical" sulfates.

**Interfacial Tension of Chemodegradable Surfactants.** The plots of equilibrium interfacial tensions $\gamma$ vs concentration (log c) of aqueous solutions of two pairs of cis-$C_n$ and trans-$C_n$ isomers containing 2-*n*-nonyl and 2-*n*-undecyl substituents, at a constant salt concentration, $m_s$ = 0.20 mol/dm$^3$, in the heptane−water system at 31 °C (Krafft point for undecyl derivative[11] is near 30 °C) are shown in Figures 2 and 3, respectively. The surface activity of the studied surfactants comprising the 1,3-dioxane moiety increases with the alkyl chain length increase. Comparison of $\gamma = f(\log c)$ curves for the cis and trans isomers of appropriate surfactants indicates that the studied isomers show different efficiency of adsorption at the heptane−aqueous NaCl interface. The trans isomers give lower oil−water interfacial tension than the cis ones at the same surfactant concentration. This behavior suggests that the trans

cis-$C_9$, trans-$C_9$, cis-$C_{11}$ and trans-$C_{11}$, respectively) were previously described.[6a] Water was twice distilled and further purified with a Mili-Q water system (Millipore). Aerosol OT [sulfosuccinic acid bis(2-ethylhexyl) ester, AOT], sodium decyl sulfate ($C_{10}OSO_3Na$), and sodium dodecyl sulfate $C_{12}OSO_3Na$) were obtained from Sigma. Their purities, as determined by the hyamine titration method,[7] were 99.5%, 99.8%, and 99.9%, respectively. No minima were observed in plots of interfacial tension against log[surfactant] (see later); such plots (Figures 2 and 3) were of the typical shape for a micelle-forming surfactant. Sodium chloride was puriss. p.a. and used as received from Fluka (aqueous solutions had surface tension in good agreement with those obtained by Aveyard and Saleem,[8] using samples roasted for 12 h at 450 °C). The *n*-heptane (Fluka purum) was passed through chromatographic alumina before use to remove polar impurities. The heptane−water interfacial tension at 31 °C was 50.1 mN m$^{-1}$, in good agreement with literature values of 50.28 mN m$^{-1}$ (at 30 °C).[9]

**Measurements.** Interfacial tensions above ca.5 mN m$^{-1}$ were measured (according to the directions given by Lunkenheimer and Wantke[10]) using a Krüss K12e processor tensiometer for solutions of surfactants in 10$^{-4}$ M aqueous NaHCO$_3$ at 31 ± 0.2 °C. The du Nouy Pt−Ir ring method was employed.

**TABLE 1: Interfacial Properties of Sodium *cis*- and *trans*-(2-*n*-Alkyl-1,3-dioxan-5-yl) Sulfates at 31 °C at the Water−Heptane Interface**

| entry | alkyl | surfactant | $\pi_{cmc}$ (mN m$^{-1}$) | $10^6\Gamma_{cmc}$ (mol m$^{-2}$) | $pC_{20}$ | $10^{20}A_{cmc}$ (m$^2$) | $10^3$cmc (mol dm$^{-3}$) | $x_{min}$ | $x_1/x_{AOT}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $n$-C$_9$H$_{19}$ | *cis*-C$_9$ | 45.0 | 3.23 ± 0.05 | 4.04 | 51.4 ± 1.2 | 3.40 ± 0.07 | 0.52 | 1.1 |
| 2 | $n$-C$_9$H$_{19}$ | *trans*-C$_9$ | 44.3 | 3.28 ± 0.07 | 4.27 | 50.6 ± 1.3 | 2.01 ± 0.03 | 0.30 | 0.43 |
| 3 | $n$-C$_{11}$H$_{23}$ | *cis*-C$_{11}$ | 45.3 | 3.23 ± 0.03 | 5.16 | 51.3 ± 1.2 | 0.216 ± 0.008 | 0.12 | 0.14 |
| 4 | $n$-C$_{11}$H$_{23}$ | *trans*-C$_{11}$ | 45.4 | 3.25 ± 0.06 | 5.44 | 51.1 ± 1.4 | 0.164 ± 0.005 | 0.06 | 0.06 |
| 5 | $n$-C$_{10}$H$_{21}$ | C$_{10}$OSO$_3$Na | 44.6 | 3.60 ± 0.08 | 3.43 | 46.1 ± 1.7 | 9.73 ± 0.09 | 0.72 | 2.8 |
| 6 | $n$-C$_{12}$H$_{25}$ | C$_{12}$OSO$_3$Na | 46.4 | 3.32 ± 0.04 | 4.78 | 50.1 ± 1.0 | 0.69 ± 0.01 | 0.18 | 0.22 |

isomers containing an equatorial sodium sulfate group have higher efficiency of adsorption than the cis isomers containing the axial sulfate group, as can be surmised by the values of the $pC_{20}$ parameter (see Table 1), which is a measure of surface or interfacial tension reduction efficiency, calculated according to definition of Rosen[12] as the negative of the logarithm of the surfactant aqueous solution concentration necessary to reduce the interfacial tension of heptane−water by $\Delta\gamma = 20$ mN m$^{-1}$. The interface tension values provided possibilities for calculating the maximum surface excess concentration ($\Gamma_{cmc}$) of surfactants at the oil−aqueous NaCl solution interface from the maximum slope using the relationship[13]

$$\Gamma_{cmc} = [d\pi/d(\ln c + \ln y_{\pm})]/fRT \tag{1}$$

where $\pi$ is the interface tension reduction in N m$^{-1}$ ($\pi = \gamma_o - \gamma$, where $\gamma_o$ is the tension of oil−water interface at 31 °C), $y_{\pm}$ is the surfactant mean activity coefficient at the cmc evaluated from the Debye−Hückel limiting law (log $y_{\pm} = -0.509J^{0.5}$), $f = 1 + 1/(1 + r)$, $r$ is the ratio between the molar concentration of added salt and the molar concentration of surfactant in the solution, $R$ is the gas constant, and $T$ is the absolute temperature. The minimum area per surfactant molecule ($A_{cmc}$) can be derived from eq 2

$$A_{cmc} = 1/(N_A\Gamma_{cmc}) \tag{2}$$

where $N_A$ is the Avogadro number. Values of the effectiveness of interface tension reduction given by $\pi_{cmc}$, the effectiveness of adsorption given by the maximum adsorption $\Gamma_{cmc}$, and minimum area per molecule $A_{cmc}$ are reported in Table 1 together with the mean errors of the surface equation of state parameters. As can be seen, $\pi_{cmc}$ slightly increases with increasing the surfactant tail length n. To examine the effect of incorporation of the six−membered 1,3-dioxane ring between the hydrophobic alkyl chain and the hydrophilic sulfate group on the interfacial tension, we have compared the surface activity of the surfactants under study with the standard type, single-tailed anionic surfactants. The plots of interfacial tension $\gamma$ vs log $c$ of aqueous solutions for the sodium $n$-decyl (C$_{10}$OSO$_3$Na) and $n$-dodecyl sulfates (C$_{12}$OSO$_3$Na) are also shown in Figures 2 and 3. It is clear from the plots that both the *cis*- and *trans*-C$_{11}$ surfactants have higher efficiency of adsorption than C$_{12}$OSO$_3$Na and both *cis*- and *trans*-C$_9$ have higher efficiency of adsorption than C$_{10}$-OSO$_3$Na, but lover efficiency of adsorption than C$_{12}$OSO$_3$Na (see Table 1 $pC_{20}$). All *cis*-C$_n$ and *trans*-C$_n$ diastereomers have almost identical surface excess concentration, $\Gamma_{cmc}$, equal to 3.2 × 10$^{-6}$ mol m$^{-2}$, i.e., nearly the same $A_{cmc}$ values. Values of the $\Gamma_{cmc}$ quoted here refer to the values obtained by the quadratic fit. However, the $\Gamma_{cmc}$ for studied surfactants are slightly smaller (the surface areas $A_{cmc}$ are greater) than for the chosen standards (Table 1). The values of standard free energy of adsorption, $\Delta G^o_{ads}$, for surfactants under study was calculated from eq 3

$$\Delta G^o_{ads} = -nRT \ln B \tag{3}$$

where $n$ is equal to the number of ions into which the molecule dissociates[14] (for univalent ionic surfactant according to Lucassen-Reynders $n = 2$) and $B$ is an equilibrium constant of the Temkin adsorption isotherm presented by eq 4[15]

$$\ln x = -\ln B + \frac{g}{RT}\pi^{1/2} \tag{4}$$

where the constant $g$ is related to the surface nonideality parameter $H_s$ and to the limiting surface excess concentration $\Gamma_{\infty}$ as

$$g = 2\sqrt{\frac{-H_s}{\Gamma_{\infty}}} \tag{5}$$

The standard states are assumed as follows: a hypothetical state in which the product of mole fraction and activity coefficient is unity for the interface, and in the bulk solution the activity coefficient is unity and the concentration of the surface-active agent is equal to the constant B. Some additional remarks on use of the Temkin-type equation and $\Delta G^o_{ads}$ equations are given in ref 15b,c. The results, together with some data concerning the air−water interface, and the mean errors of the surface equation of state parameters are collected in Tables 1 and 2. The $\Delta G^o_{ads}/CH_2$ values are significantly higher in comparison to those reported previously.[16] However, the authors, by assuming $n = 1$ in calculation of the $\Delta G^o_{ads}$ did not differentiate the adsorption process for the ionic and the nonionic surfactants. On the other hand, Lucassen-Reynders, assuming charge neutrality in the adsorption layer, proposed to take into account the participation of both species, i.e., surface-active anion and counterion in adsorption process by introducing the coefficient "2" to the equation for $\Delta G^o_{ads}$ for univalent ionic amphiphiles (as is the case of our studied surfactants).

Standard free energy of micellization, $\Delta G^o_{cmc}$, was calculated according to eq 6.[17]

$$\Delta G^o_{cmc} = (2 - \alpha)RT \ln x_{\pm cmc} \tag{6}$$

where $x_{\pm cmc} = x_{cmc}y_{\pm}$ and is the standard mean activity, where $x_{cmc}$ is the mole fraction of surfactant at the cmc and $\alpha$ is the micellar degree of dissociation. The values of $\alpha$ (included in Table 2) were extracted from the surface tension measurements of the aqueous surfactant and NaCl solutions according to procedure described in ref 18. Assuming the total free energy change is divisible into independent additive contributions from the component part of the amphiphile molecule according to eq 7, it is possible to calculate the increments $\Delta G^o_{ads}/CH_2$ and $\Delta G^o_{mic}/CH_2$ by comparing the total $\Delta G^o_{ads}$ or $\Delta G^o_{mic}$ for homologous compounds.

$$\Delta G^o = \Delta G^o(CH_3-) + (n-1)\Delta G^o(-CH_2-) + \Delta G^o(-Y) \tag{7}$$

where

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**TABLE 2: Standard Free Energies of Adsorption and Micellization of Diastereomeric Sulfates *cis*-C$_n$ and *trans*-C$_n$ and Sodium *n*-Alkyl Sulfates C$_n$OSO$_3$Na at 31 °C**

| entry | surfactant | interface | isomer | α | $-\Delta G^\circ_{ads}$ (kJ mol$^{-1}$) | $-\Delta G^\circ_{ads}$/CH$_2$ (kJ mol$^{-1}$) | $-\Delta G^\circ_{cmc}$ (kJ mol$^{-1}$) | $-\Delta G^\circ_{cmc}$/CH$_2$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| 1 | *cis*-C$_9$ | heptane−water | cis | 0.30 | 106.4 ± 0.8 | 6.8 | 44.0 ± 0.6 | 6.2 |
| 2 | *cis*-C$_{11}$ | heptane−water | cis | 0.28 | 120.1 ± 0.9 | | 56.5 ± 0.7 | |
| 3 | *cis*-C$_9$ | air−water | cis | 0.30 | 63.7 ± 0.5[a] | 4.0 | 36.1 ± 0.1[b] | 3.2 |
| 4 | *cis*-C$_{11}$ | air−water | cis | 0.28 | 71.8 ± 0.6[a] | | 42.5 ± 0.3[b] | |
| 5 | *trans*-C$_9$ | heptane−water | trans | 0.30 | 114.2 ± 0.7 | 6.6 | 46.2 ± 0.6 | 5.8 |
| 6 | *trans*-C$_{11}$ | heptane−water | trans | 0.28 | 127.6 ± 0.9 | | 57.7 ± 0.7 | |
| 7 | *trans*-C$_9$ | air−water | trans | 0.30 | 67.9 ± 0.4[a] | 3.3 | 38.2 ± 0.2[b] | 3.0 |
| 8 | *trans*-C$_{11}$ | air−water | trans | 0.28 | 74.5 ± 0.5[a] | | 44.1 ± 0.4[b] | |
| 9 | C$_{10}$OSO$_3$Na | heptane−water | | 0.36[c] | 99.2 ± 0.6 | 7.9 | 38.1 ± 0.3 | 6.1 |
| 10 | C$_{12}$OSO$_3$Na | heptane−water | | 0.32[c] | 115.1 ± 0.8 | | 50.2 ± 0.7 | |
| 11 | C$_{10}$OSO$_3$Na | air−water | | 0.36[c] | | | 30.7 ± 0.2[d] | 3.3 |
| 12 | C$_{12}$OSO$_3$Na | air−water | | 0.32[c] | | | 37.3 ± 0.1[d] | |

[a] Taken from ref 6a. [b] The cmc values have been previously reported in ref 6a. [c] Calculated using equation α = 1 − β and β values reported in ref 20. [d] Calculated using the data reported in ref 21.





**Figure 4.** Effect of sodium *cis*-, *trans*-, and *cis/trans*- mixture of (2-*n*-nonyl-1.3-dioxan-yl) sulfates and *n*-decyl sulfates on γ$_c$ in AOT/*n*-heptane/aqueous NaCl system: *cis*-C$_9$, *trans*-C$_9$, *cis/trans*-C$_9$ (60/40 wt % mixtures), and C$_{10}$OSO$_3$Na. $m_{AOT} = 4.6 \times 10^{-4}$ M, NaCl 0.1 M at 31 °C.
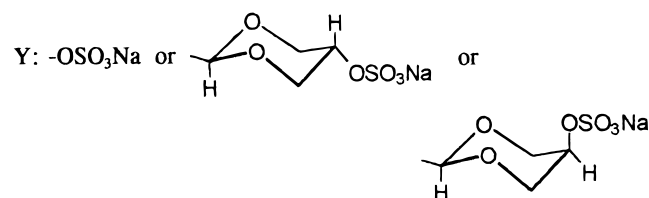
The same approach has previously been applied and frequently described.[15b,19] The increments of the standard free energies of adsorption, $\Delta G^\circ_{ads}$/CH$_2$, and micellization, $\Delta G^\circ_{cmc}$/CH$_2$, calculated for one methylene group, −CH$_2$−, of alkyl chain C$_n$ are presented in Table 2. These values refer to the sodium *cis*- and *trans*-(2-*n*-alkyl-1,3-dioxan-5-yl) sulfates and sodium *n*-alkyl sulfates, respectively. We confronted the $\Delta G^\circ_{ads}$ values with those of standard surfactants. As can be seen, the $-\Delta G^\circ_{ads}$ values for the 2,5-disubstituted 1,3-dioxanes are much higher than for the respective C$_n$OSO$_3$Na homologues. Moreover, the higher efficiency of adsorption of the trans isomers than that of the cis ones is evident. The values of ($\Delta G^\circ_{ads}$/CH$_2$) differ for both kinds of diastereomeric surfactants as well; however, these differences are not crucial. Our observations enable us to suggest that the 1,3-dioxane moiety is equivalent, approximately, to 1.5 and 2.4 methylene units of the hydrocarbon chain for cis and trans isomers, respectively.

**Interfacial Tension Minima.** We investigated the variation of tension γ$_c$ with the mole fraction, $x$ [$x = m_1/(m_1 + m_{AOT})$], of pure sodium *cis*- and *trans*-(2-*n*-alkyl-1,3-dioxolan-5-yl) sulfates and sodium alkyl sulfates (the sulfate concentration was $m_1$) in their mixtures with AOT (at a fixed concentration, $m_{AOT} = 4.6 \times 10^{-4}$ M), close to and above its cmc in the system containing heptane and aqueous NaCl and sufficient to form Winsor II system[1d]). In all cases the NaCl concentration was 0.1 M at 31 °C. The applied sulfates (i.e., the so-called "second" surfactants) can be characterized by $a_h/a_c$ in the pure film. The formation of the mixed surfactant film with AOT may create the curvature changes sign, i.e., from negative to positive (the Winsor II−Winsor I inversion). This finding has recently been discussed by Aveyard et al.[1d] for the heptane−aqueous NaCl solution−AOT−SDS system, in which $x_{min}$ at the ultralow interfacial tension being equal to 0.21 and corresponding to inversion of the w/o into o/w microemulsion was achieved.

As shown in Figure 6 the alkyl chain length increase of both *cis*-C$_n$ and C$_n$OSO$_3$Na influences significantly the concentration value $x_{min}$ at which the ultralow interfacial tensions, γ$_{c,min}$, occur. In all cases, the hydrophobicity increase of single chain surfactants promotes the formation of the mixed adsorbed films. The values of $x_{min}$ appropriate for the w/o into o/w microemul-
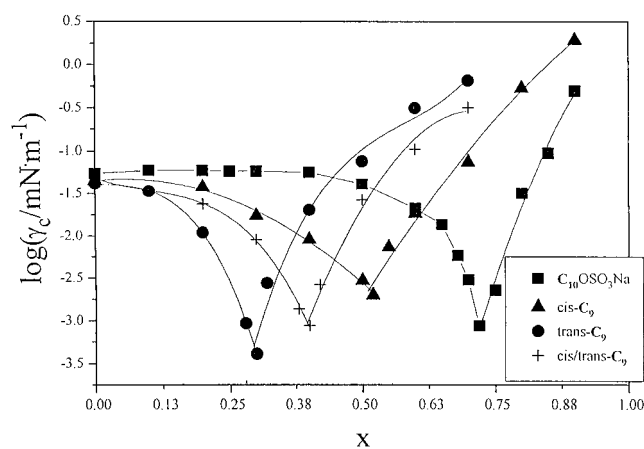
sion inversion are as 0.52, 0.12, 0.72, and 0.18, respectively, for the cis-C$_9$ and cis-C$_{11}$ isomers and for C$_{10}$OSO$_3$Na and C$_{12}$-OSO$_3$Na. Thus, the film curvature change from negative to positive is undergone for the longer alkyl chain sulfates at lower concentrations. Recall that surfactants of higher hydrophobicity show a stronger tendency to form mixed films with AOT and more effectively change the $a_h/a_c$ assuming the monomolecular layer formation. Further studies on $x_{min}$ of the *cis/trans*-C$_{11}$ and cis/trans-C$_9$ mixtures (Figures 4 and 5) as the second surfactant did not reveal any synergetic effect among the diastereomeric compounds.

The effect of OSO$_3$Na group configuration on the interfacial tension of the studied surfactant mixtures (Figures 5 and 6) can be related to the effective alkyl chain length of diastereomeric surfactants. Among the studied surfactants, the trans forms are more effective than the cis ones considering both the $x_{min}$ concentration and the ultralow tension values γ$_{c,min}$. The single-chain surfactant addition to the heptane−0.1 M NaCl$_{aq}$−AOT system renders $a_h = a_c$ (i.e., the mean head and tail area of surfactants in a mixed film are equal), and ultralow values of tension (γ$_{c,min}$) occur as a result of surfactant transfer to the surfactant middle phase. Since the sodium sulfate group is intrinsically large, further increase of diastereomeric surfactant (or sodium alkyl sulfate) concentration increases $a_h/a_c$ from 1 to greater than unity to give o/w microemulsion droplets. The results from Figures 5 and 6 permit us to suggest that the effective $a_h/a_c$ for the trans isomers/AOT mixture is higher than that for the cis isomers/AOT mixture. *trans*-C$_{11}$ and cis-C$_{11}$ are

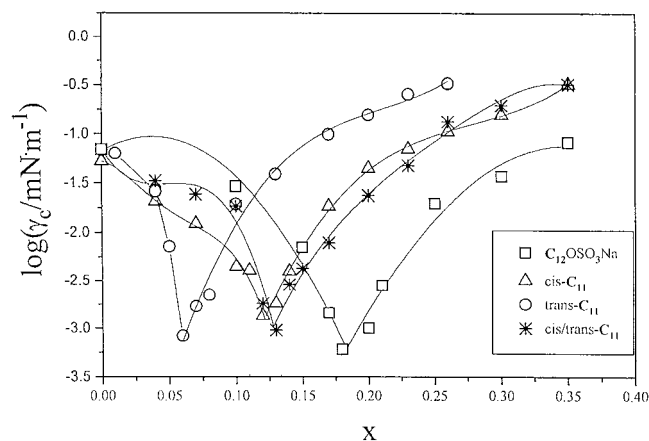**Figure 5.** Effect of sodium *cis-*, *trans-*, and *cis/trans-* mixture of (2-*n*-undecyl-1.3-dioxan-yl) sulfates and *n*-dodecyl sulfates on $\gamma_c$ in AOT/*n*-heptane/aqueous NaCl system: *cis-*$C_{11}$, *trans-*$C_{11}$, *cis/trans-*$C_{11}$ (90/10 wt % mixtures), and $C_{12}OSO_3Na$. $m_{AOT} = 4.6 \times 10^{-4}$ M, NaCl 0.1 M at 31 °C.
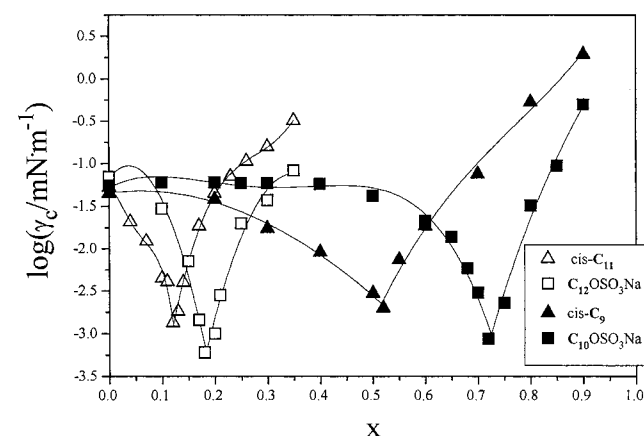


**Figure 6.** Effect of sodium cis-(2-*n*-alkyl-1.3-dioxan-yl) sulfates and *n*-alkyl sulfates on $\gamma_c$ in systems containing AOT, *n*-heptane, and aqueous NaCl: *cis-*$C_{11}$, $C_{12}OSO_3Na$, *cis-*$C_9$, and $C_{10}OSO_3Na$. $m_{AOT} = 4.6 \times 10^{-4}$ M, NaCl 0.1 M at 31 °C.

more efficient than $C_{12}OSO_3Na$ because of their higher hydrophobicity introduced by the 1,3-dioxane ring (see respective values of $\Delta G^o_{ads}$ in Table 2). According to the literature, as the second surfactant is added to the system, the w/o droplets grow in size until the microemulsion inverts. The influence of the 1,3-dioxane ring present in the second surfactant structure upon the $a_h/a_c$ modification and the phase behavior can be readily explained in terms of the hydrophilic group axial and equatorial configuration.

## Conclusions

The main conclusions from this study are as follows.

Adsorption of single-tailed sodium *cis-* and *trans-*(2-*n*-alkyl-1,3-dioxan-yl) sulfates at heptane–aqueous NaCl interfaces is favored by (i) increase in alkyl chain length, and (ii) change of polar sodium sulfate group configuration at the C-5 carbon atom of the 1,3-dioxane ring.

The cmc, $\Delta G^o_{ads}$ and $\Delta G^o_{cmc}$ values are lower for the trans isomers than for the cis ones; the effectiveness of surface tension reduction is nearly the same for both diastereoisomers.

Addition of *cis-*$C_n$ and *trans-*$C_n$ sulfates to the w/o microemulsion droplets containing AOT + NaCl can result in ultralow oil–water interfacial tensions. The effect of a diastereomeric second surfactant is as expected, but trans analogues are more effective than the cis homologues at promoting the Winsor II–Winsor III–Winsor I transitions. The molar ratios (second surfactant/AOT) in the droplets required for minimum tension are 0.43 and 1.1 for *trans-*$C_9$ and *cis-*$C_9$ isomers and 0.06 and 0.14 for *trans-*$C_{11}$ and *cis-*$C_{11}$ isomers and for comparison the appropriate findings for $C_{10}OSO_3Na$ and for $C_{12}OSO_3Na$ are 2.8 and 0.22, respectively.

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