

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/27695097>

Adsorption of sodium dodecyl sulfate and cosurfactant at the planar cyclohexane-brine interface. Validity of the saturation adsorption approximation and effects of the cosurfactant...

ARTICLE *in* LANGMUIR · JANUARY 1993

Impact Factor: 4.46 · DOI: 10.1021/la00025a048 · Source: OAI

CITATIONS

26

READS

57

6 AUTHORS, INCLUDING:



[George van Aken](#)

NIZO food research

137 PUBLICATIONS 2,371 CITATIONS

SEE PROFILE

Adsorption of Sodium Dodecyl Sulfate and Cosurfactant at the Planar Cyclohexane-Brine Interface. Validity of the Saturation Adsorption Approximation and Effects of the Cosurfactant Chain Length

W. K. Kegel, G. A. van Aken,[†] M. N. Bouts, H. N. W. Lekkerkerker,^{*}
J. Th. G. Overbeek, and P. L. de Bruyn

Van't Hoff Laboratory, University of Utrecht, Padualaan 8,
3584 CH Utrecht, The Netherlands

Received April 22, 1992. In Final Form: September 8, 1992

The interfacial excess concentrations of sodium dodecyl sulfate (SDS) and two different cosurfactants (pentanol and hexanol) in mixed monolayers at the interface between water (with 0.2 M NaCl) and an oil phase consisting of cyclohexane and cosurfactant are determined from surface tension measurements using the Gibbs adsorption equation. The data are analyzed in two ways: assuming saturation adsorption and fitting the data to the Szyszkowski equation. This analysis reveals that a constant interfacial concentration in the vicinity of the critical micelle concentration is a good approximation even though the cosurfactant interfacial concentration does not reach its saturation value in the experimental cosurfactant concentration range. For both pentanol and hexanol, at low concentrations a strong competition between cosurfactant and SDS is observed, whereas at higher concentrations the composition of the interface remains practically constant. Under these conditions a high packing density in the mixed monolayer is observed.

Introduction

The area of the interface water-oil is an important quantity in microemulsion theory.¹⁻⁴ This area is generated and stabilized by the adsorption of surfactant (and cosurfactant, if applicable). Therefore it is important to know the interfacial concentrations of the surfactant.

We have studied a model system composed of brine (aqueous salt solution), cyclohexane, ionic surfactant (sodium dodecyl sulfate, SDS) and a nonionic cosurfactant (an alcohol). By variation of the salt and cosurfactant concentration and the chain length of the cosurfactant, we can regulate some properties of the interface which serve as input parameters in the above mentioned theories.

Examination of the phase behavior using equal volumes of brine and oil for the two alcohols pentanol and hexanol revealed some large differences. Details are reported in ref 5. In this article, we report the determination of the interfacial concentrations of SDS and the alcohols as a function of SDS and cosurfactant activities at constant salt concentration. We also address the question whether or not the apparently different interfacial properties are accompanied by a difference in composition of the interface.

For systems containing pentanol, the interfacial excess concentrations have been determined by Verhoeckx et al.⁶ Since this work we have obtained better numbers based on improved techniques and improved interpretation.

We have determined the interfacial excess concentration, Γ_i , by using the Gibbs adsorption equation

$$\left(\frac{\partial \gamma}{\partial \ln(a_i)} \right)_{a_j \neq i, k, T, P} = -RT\Gamma_i \quad (1)$$

on measurements of the interfacial tension γ between water and oil obtained with the spinning drop method. In eq 1 a_i and Γ_i are the activity and the interfacial concentration of component i , respectively, a_k and a_l are the activities of two reference components (e.g. water and cyclohexane), and R , T , and P have their usual meaning. Since the interfacial tension of water-oil is very low under conditions where microemulsions can be formed, the measurements from which the slope of γ vs $\ln(a_i)$ is determined must be carried out at low to very low interfacial tensions.

From (1) it follows that in order to determine the interfacial concentration, we need to know the interfacial tensions as a function of the activities in a bulk phase $\gamma(\ln(a_i))$. In the case of systems containing only one surface-active solute, saturation adsorption is often found in the vicinity of the cmc and the interfacial concentration is obtained by fitting the data points to a straight line. In this paper, a system containing two surface-active components is studied. Interfacial tensions of this kind of systems are often also interpreted as if saturation adsorption occurs in the neighborhood of the cmc.⁶⁻⁸ Here we will avoid this assumption by fitting the data to the Szyszkowski equation and compare the results with the assumption of saturation adsorption. The equation

$$\gamma_0 - \gamma = B \ln \left(\frac{c_i}{A} + 1 \right) \quad (2)$$

in which γ_0 is the interfacial tension at which $c_i = 0$, $B = RT\Gamma_{i,\infty}$, and $\Gamma_{i,\infty}$ is the saturation adsorption, was originally stated by Szyszkowski⁹ on purely empirical grounds and its validity appears to be quite broad.^{10,11} As shown by Rosen and Aronson,¹⁰ (2) appears to fit data points

^{*} Author to whom correspondence should be addressed.

[†] Present address: Department of Biophysical Chemistry, Netherlands Institute for Dairy Research (NIZO), P.O. Box 20, 6710 BA Ede, The Netherlands.

(1) Overbeek, J. Th. G.; Verhoeckx, G. J.; de Bruyn, P. L.; Lekkerkerker, H. N. W. *J. Colloid Interface Sci.* 1987, 119, 422.

(2) Andelman, D.; Cates, M. E.; Roux, D.; Safran, S. A. *J. Chem. Phys.* 1987, 87, 7229.

(3) Widom, B. *Langmuir* 1987, 3, 12.

(4) Golubovic, L.; Lubensky, T. C. 1990, *Phys. Rev. A* 41, 4343.

(5) Kegel, W. K.; Lekkerkerker, H. N. W., In preparation.

(6) Verhoeckx, G. J.; de Bruyn, P. L.; Overbeek, J. Th. G. *J. Colloid Interface Sci.* 1987, 119, 409.

(7) Aveyard, R.; Binks, B. P.; Mead, J. *J. Chem. Soc. Faraday Trans. 1* 1987, 83, 2347.

(8) Zhou, J. S.; Dupeyrat, M. *J. Colloid Interface Sci.* 1990, 134, 320.

(9) von Szyszkowski, B. *Z. Phys. Chem.* 1908, 64, 385.

(10) Rosen, M. J.; Aronson, S. *Colloids Surf.* 1981, 3, 201.

(11) Van Hunsel, J.; Joos, P. *Langmuir* 1987, 3, 1069. Joos, P.; Vollhardt, D.; Vermeulen, M. *Langmuir* 1990, 6, 524.

reasonably well as long as the surface pressure exceeds 20 mN/m and $c/A \gg 1$.

As already shown independently by Frumkin and Haber¹² in the 1920s, (2) is easily derived by combining the Langmuir adsorption equation

$$\Gamma(c_i) = \Gamma_{i,\infty} \frac{c_i}{A + c_i} \quad (3)$$

with the Gibbs equation (1). The "fitparameter" A can thus be regarded as the ratio of the desorption and adsorption rate constants.

Several attempts have been made¹³⁻¹⁵ to derive (2) from more fundamental concepts, which will not be discussed here.

Experimental Section

Materials. Sodium dodecyl sulfate (SDS) was "specially pure" grade from BDH. It was purified by recrystallization in ethanol (2 times) and was stored in a vacuum desiccator over silica gel. Immediately before use, it was dissolved in water and filtered through a C18-silica column (SEP-pak cartridge, Millipore, pretreated with methanol and water).

Cyclohexane, 1-pentanol, 1-hexanol, and NaCl were Baker "analyzed" reagents and were used without further purification. Deionized water was distilled 3 times before use.

Sample Preparation. An 8.00-g portion of initial oil phase was carefully poured on 10.00 g of initial water phase in 25-mL glass tubes with Teflon-sealed screw caps. The initial oil phase was a solution of 1-pentanol or 1-hexanol in cyclohexane, with different initial mass fractions, and the water phase was a 0.20 M NaCl solution containing various amounts of SDS. Equilibrium was attained by gently rolling the samples on a roller bench (ca. 1 rev/min). Shaking or rolling too fast promotes the formation of unstable coarse emulsions or liquid crystalline phases that may persist for quite a long period of time.¹⁶

Analysis of the Equilibrated Phases. Pentanol and hexanol concentrations in the oil and water phase were measured with a Packard Model 433 gas chromatograph equipped with a flame ionization detector and a glass column packed with cross-linked polystyrene resin. The SDS concentration in the water phase was determined colorimetrically^{17,18} for every sample. An excess quantity of methylene-blue was added to a water sample containing SDS. The equimolar complex was extracted with chloroform and the extinction was measured at 652 nm using a Bausch and Lomb/Shimadzu Spectronic 200-UV spectrophotometer. The detection limit is approximately 10^{-7} M in the original water phase. The possible presence of (a small amount of) water and SDS in the oil phase does not have any influence on the analysis.

Interfacial Tensions. Interfacial tensions between the water and oil phases were measured by the use of the spinning drop technique. The apparatus was built in our laboratory.¹⁶ It enables one to measure interfacial tensions between approximately 10^{-4} and 10^2 mN/m. A precision glass tube (internal diameter 4 mm, length 95 mm, Teflon sealed) is rotated at high speed (up to 12 000 rpm). Inside the tube, a small drop of the less dense phase is introduced into the denser phase. Drop dimensions were measured by moving a microscope with cross-threads fixed to the eye piece by means of a pair of calibrated translators. Correction for refraction of light was carried out. The glass tube was thermostated because of the heat produced by the friction of the ball bearings. The interfacial tension was calculated from the length, l , and the maximum diameter, d , of the rotating drop (see Figure 1).

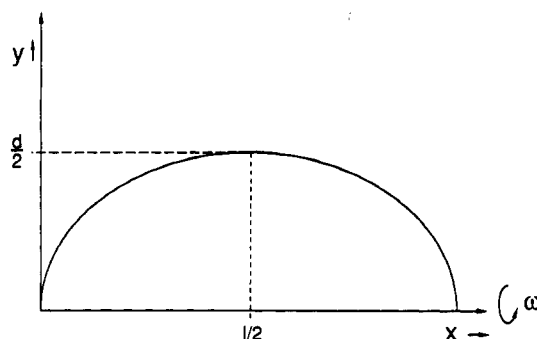


Figure 1. Coordinate system for a drop in the spinning drop tensiometer.

By equating the pressure difference inside and outside a drop in a centrifugal field to the capillary pressure across the interface, Princen et al.¹⁹ find the following differential equation for the shape

$$\frac{dX}{dY} = \frac{Y(1 - \alpha Y^2/4)}{(1 - Y^2(1 - \alpha Y^2/4)^2)^{1/2}} \quad (4)$$

Here the dimensionless variables X and Y are defined in units of r_o , the radius of curvature at $(x = 0, y = 0)$

$$X = x/r_o; Y = y/r_o \quad (5)$$

Further the dimensionless shape parameter

$$\alpha = \frac{\Delta\rho\omega^2 r_o^3}{2\gamma} \quad (6)$$

where $\Delta\rho$ is the density difference between the two phases, ω the angular velocity of rotation, and γ the interfacial tension. Now (4) can be solved numerically to yield $X_o = l/2r_o$ and $Y_o = d/2r_o$ for any α . We used a numerical procedure to obtain α corresponding to the experimentally observed ratio $Y_o/X_o = l/d$. From the corresponding X_o and Y_o , r_o can immediately be calculated and γ follows from (6). The interfacial tensions obtained in this way were compared to literature values and showed good agreement.¹⁶

Fitting Data to the Szyszkowski Equation. A Levenberg-Marquardt algorithm was used²⁰ and convergence was usually reached within less than 10 iterations.

Determination of Cosurfactant Activities from Their Distribution between the Oil and Water Phase. At equilibrium the distribution constant K^o and the experimentally accessible distribution coefficient K are related by

$$K = \frac{x^o}{x^w} = K^o \frac{f^w}{f^o} \quad (7)$$

where the superscripts w and o refer to the water and oil phase, respectively, and x and f are the fractions (mass, mole, or whatever) and the activity coefficients of the cosurfactant. Measurement of K as a function of the cosurfactant fraction in the oil phase revealed that the data could be well described by

$$K = D + E \frac{x^o}{1 + x^o} \quad (8)$$

Results for pentanol and hexanol are presented in Figure 2.

Since salt is hardly soluble in the oil phase, we assume that the activity of the cosurfactant in the oil phase is independent of the salt concentration in the water phase and further that $f^w = 1$ at $c^w_{NaCl} = 0$, at the low cosurfactant concentrations such as occur in the water phase. At finite salt concentrations, f^w appears to be larger than 1; the cosurfactant is salted out. As $x^o \rightarrow 0$, $f^o \rightarrow 1$ and thus

(12) Freundlich, H. *Kapillarchemie*; Akademische Verlagsgesellschaft m.b.h.: Leipzig, 1930; Band I, Vierte Auflage, pp 77-79.

(13) Defay, R.; Prigogine, I. *Surface Tension and Adsorption*; Longmans: London, 1966; p 187.

(14) van den Tempel, M.; Lucassen, J.; Lucassen-Reynders, E. H. J. *Phys. Chem.* 1965, 69, 1798.

(15) Ross, S.; Morrison, I. D. J. *Colloid Interface Sci.* 1983, 91, 244.

(16) van Aken, G. A. Thesis Rijksuniversiteit Utrecht, 1990.

(17) Fossil Energy, U.S. Department of Energy, BC/20009-8, C9 (1980).

(18) Reid, V. W.; Longmans, G. F.; Heinert, E. *Tenside* 1967, 4, 292.

(19) Princen, H. M.; Zia, I. Y. Z.; Mason, S. G. J. *Colloid Interface Sci.* 1967, 23, 99.

(20) Press, W. H.; Flannery, B. P.; Teukolsky, S. A. and Vetterling, W. T. *Numerical Recipes*; Cambridge University Press: Cambridge, 1987; Chapter 14.

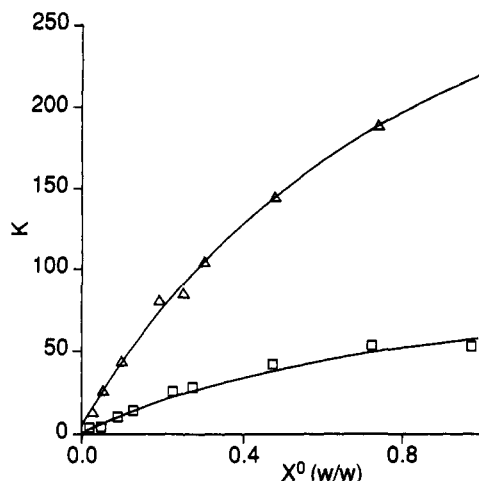


Figure 2. Distribution coefficient K of pentanol (\square) and hexanol (Δ) between cyclohexane and brine at a NaCl concentration of 0.20 M. x^0 is the mass fraction in the oil phase after equilibration. Drawn lines represent the least-squares fit according to eq 8.

$$\lim_{x^0 \rightarrow 0} K = K^0 f^w = D \quad (9)$$

Dividing (8) on both sides by D we immediately obtain the activity coefficient of the cosurfactant in the oil phase

$$\frac{1}{f^o} = 1 + \frac{E}{D} \frac{x^o}{1 + x^o} \quad (10)$$

which is enough for the determination of the surface excess as the activities can now be calculated. The activity coefficient in the water phase can also be determined. In Figure 3 results of K as a function of the salt concentration are given. Figure 3 shows a linear dependence of K on the salt concentration. We therefore define a salting out constant k^w which will be the only quantity which takes into account the nonideality of the cosurfactant in the water phase

$$f^w = 1 + k^w c^w_{\text{NaCl}} \quad (11)$$

In ref 16 the validity of (11) was verified by measuring the interfacial tension of a system containing cosurfactant, water, and salt as a function of the salt concentration. By use of the measured value of k^w (Table I), the cosurfactant interfacial concentration agreed with the one obtained by variation of the cosurfactant concentration. Equilibrium cosurfactant activities were calculated from the initial fractions in oil iteratively by (8), (7), and (11) and mass conservation within the experimental error range. Values for the coefficients D , E , and k^w are presented in Table I. The value of k^w in the pentanol system (0.62 ± 0.03) is in good agreement with the one obtained in a system containing dodecane instead of cyclohexane (0.616).²¹

Activity coefficients have also been obtained by IR spectroscopy and by osmometry.²² Comparison with our results reveals that these appear to be weakly dependent on the alcohol chain length and the nature of the hydrocarbon. For example at an alcohol concentration of 0.05 mol/dm³ the activity coefficients are 0.700 for pentanol in cyclohexane (this work), 0.735 for hexanol in cyclohexane (this work), 0.811 for octanol in *n*-octane,²² and 0.792 for dodecanol in *n*-octane.²² The strongest nonideality in the above series occurs for pentanol which is a reflection of its more polar character.

From Table I and (10) it follows that the tendency of the cosurfactant to reside into the oil phase is strongly influenced by the amount of cosurfactant already present, an indication of a multiassociation equilibrium. In the limit of small concentrations, pentanol has a slight preference for the water phase but hexanol is already nearly 5 times more soluble in the oil phase.

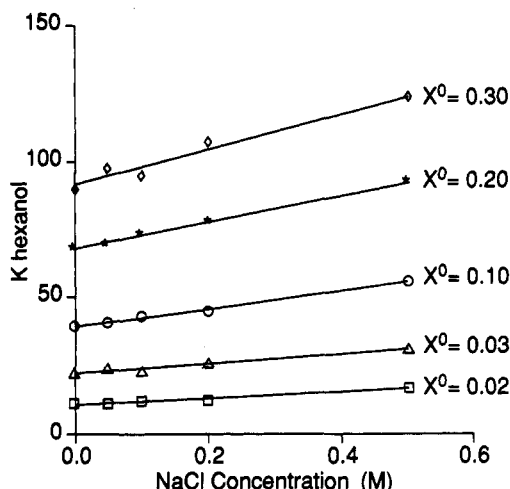
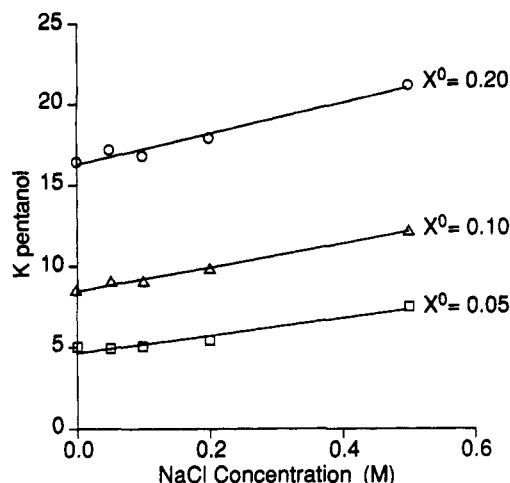


Figure 3. Distribution coefficient K as a function of the salt concentration for a few equilibrium pentanol (a, top) and hexanol (b, bottom) mass fractions in the oil phase. Mass fractions are indicated in the figures.

Table I. Values for the Distribution Coefficients of the Cosurfactants Pentanol and Hexanol^a

	pentanol	hexanol
D	0.86	4.9
E	104.9	433.1
k^w /(mol/L)	0.62 ± 0.03	0.72 ± 0.02

^a D and E (eq 8) were determined at 0.2 M NaCl and k^w is the mean value obtained for initial weight fractions of cosurfactant in cyclohexane between 0.02 and 0.30.

Results and Analysis

Parts a and b of Figure 4 show the interfacial tensions as a function of the logarithm of the SDS concentration in the aqueous phase at different initial weight fractions of pentanol and hexanol, respectively. Because of the low SDS concentration in the water phase, the SDS activity coefficient at concentrations below the cmc was assumed not to vary with the SDS concentration.

Except for the isotherm representing the initial pentanol weight fraction of 20%, the Szyszkowski equation appears to fit the data points quite well. In the case of low initial cosurfactant concentrations ($\leq 7.5\%$), a good fit was obtained over the whole range of SDS concentrations used, even when $C_{\text{SDS}} = 0$ is taken into account. At higher concentrations the shape of the isotherm apparently becomes more "curved", indicating a stronger adsorption gradient in a comparable SDS concentration range, and

(21) Aveyard, R.; Heselden, R. *J. Chem. Soc., Faraday Discuss.* 1975, 71, 312.

(22) Aveyard, R.; Briscoe, R. J.; Chapman, J. *Trans. Faraday Soc.* 1973, 69, 1772.

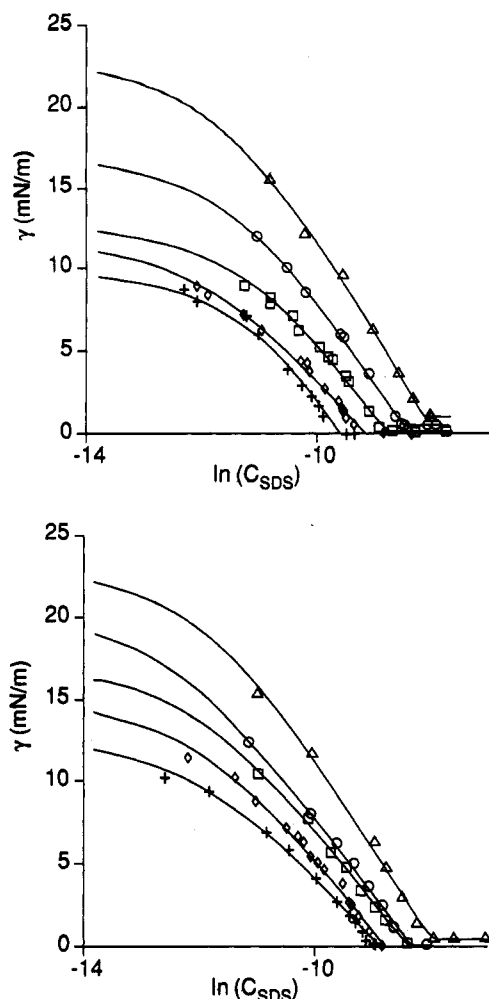


Figure 4. Interfacial tensions between oil and water in the presence of SDS, salt, and pentanol (a, top) or hexanol (b, bottom) as a function of the SDS concentration in the water phase. Symbols Δ , \circ , \square , \diamond , and $+$ correspond to initial mass fractions of 0.01, 0.02 (a) or 0.03 (b), 0.05, 0.10, and 0.20 (w/w), respectively. The isotherm corresponding to 0.075 (w/w) hexanol is not shown. The salt concentration in the water phase is 0.20 M. Solid lines correspond to Szyszkowski fits (as long as $c_{\text{SDS}} < \text{cmc}$).

a good fit could only be obtained without the point ($C_{\text{SDS}} = 0$, γ_0). The reason for this is not understood.

The shape of the adsorption isotherm corresponding to 10% pentanol in the oil phase (Figure 4a) is somewhat deviating compared to the other ones. Comparing the results with those reported in ref 16 shows that this behavior at this particular pentanol concentration is reproducible. Comparing parts a and b of Figure 4 reveals that systems containing pentanol apparently form micelles or microemulsions at significantly lower SDS concentrations in water over the whole range of initial cosurfactant concentrations than the systems containing the same concentrations of hexanol in the oil phase. The cmc's as well as the cosurfactant activities in the water phase are listed in Table II. From Table II it is clear that at equal concentrations of pentanol and hexanol in the oil phase pentanol has a larger effect on the value of the cmc of SDS because of its higher activity in the water phase.

In Table III single component adsorptions are given and a comparison is made between the SDS adsorptions assuming saturation adsorption in the vicinity of the cmc (i.e. fitting those data points to a straight line) and calculating the interfacial concentrations at the cmc using the coefficients from the Szyszkowski fit according to (2). The number of points in Figure 4 used for the linear fits

Table II. cmc Values of SDS and Cosurfactant Activities in the Water Phase (0.2 M NaCl) as a Function of Initial Weight Fractions of Cosurfactant in the Oil Phase

initial mass fraction	pentanol		hexanol	
	cmc (mmol/L)	a (mol/L)	cmc (mmol/L)	a (mol/L)
0.00	0.605	0.000	0.605	0.000
0.01	0.283	0.043	0.310	0.011
0.02	0.201	0.067		
0.03			0.227	0.018
0.05	0.139	0.092	0.208	0.022
0.075			0.173	0.024
0.100	0.098	0.107	0.146	0.025
0.200	0.068	0.124	0.125	0.029

Table III. SDS Interfacial Excess Concentrations Assuming Saturation Adsorption ($\Gamma_{\text{lin}}^{\text{SDS}}$), Number of Points at SDS Concentrations in the Water Phase Lower Than the cmc Used for the Linear Fit (no. of points), Interfacial Concentrations at the cmc ($\Gamma_{\text{asy}}^{\text{SDS}}$), and Saturation Interfacial Concentrations ($\Gamma_{\text{SDS},\infty}$) Resulting from Fitting Data to Equation 2 as a Function of Initial Cosurfactant Weight Fractions in Cyclohexane (x°_{init})^a

x°_{init} (w/w)	$\Gamma_{\text{lin}}^{\text{SDS}}$	no. of points	$\Gamma_{\text{asy}}^{\text{SDS}}$	$\Gamma_{\text{SDS},\infty}$
Pentanol				
0.01	2.54 ± 0.02	4	2.44 ± 0.20	2.52 ± 0.07
0.02	2.10 ± 0.05	5	2.12 ± 0.06	2.24 ± 0.03
0.05	2.01 ± 0.07	6	1.90 ± 0.12	2.10 ± 0.07
0.10	1.81 ± 0.07	8	1.65 ± 0.21	1.66 ± 0.08
0.20	1.76 ± 0.03	7	1.60 ± 0.17^b	1.76 ± 0.06^b
Hexanol				
0.01	2.70 ± 0.10	4	2.27 ± 0.19	2.34 ± 0.07
0.03	2.17 ± 0.06	5	1.92 ± 0.11	1.95 ± 0.03
0.05	1.81 ± 0.07	5	1.83 ± 0.12	1.88 ± 0.04
0.075	1.85 ± 0.05	6	1.91 ± 0.15	1.91 ± 0.06
0.10	1.86 ± 0.03	8	1.79 ± 0.15	1.87 ± 0.05
0.20	1.71 ± 0.05	7	1.58 ± 0.10	1.60 ± 0.04
pure SDS	(3.62 ± 0.04)		3.44 ± 0.19	3.45 ± 0.05

Pure pentanol: $\Gamma_p = 4.71 \pm 0.12^c$

Pure hexanol: $\Gamma_h = 4.65 \pm 0.14^c$

^a The NaCl concentrations in the water phase is 0.2 M. All interfacial concentrations are an $\mu\text{mol/L}$. ^b Only the data points in the vicinity of the cmc were fit. ^c No Szyszkowski fit was carried out; a plot of γ versus $\ln(a_{\text{co}})$ with a_{co} ranging from 0.01 to 0.05 M in water yields a straight line, indicating that saturation adsorption is already attained at very low cosurfactant concentrations.

is also indicated. It is clear that these results are highly comparable. Although strictly speaking the deviation from saturation adsorption (the value B/RT) at the cmc is not significant, the trend is about 2–5% lower. From Table III it follows that the interfacial concentration of SDS as a function of cosurfactant concentration at cosurfactant weight fractions higher than about 0.05 is almost constant, which implies, using a Maxwell relation emerging from (1)

$$\left(\frac{\partial \Gamma_{\text{co}}}{\partial \ln(a_{\text{SDS}})} \right)_{a_{\text{co}}} = \left(\frac{\partial \Gamma_{\text{SDS}}}{\partial \ln(a_{\text{co}})} \right)_{a_{\text{SDS}}} \quad (12)$$

that the cosurfactant interfacial concentration as a function of the SDS concentration is also constant. The cosurfactant interfacial concentrations are obtained by interpolating the γ - $\ln(C_{\text{SDS}})$ curves at several SDS concentrations and fitting the data to the Szyszkowski equation (2) where the cosurfactant activity instead of its concentration in the water phase c_i was used.

Results for the highest SDS concentration at which no cmc is exceeded (0.065 mol/L for systems with pentanol and 0.123 mol/L for systems with hexanol) are shown in Figure 5.

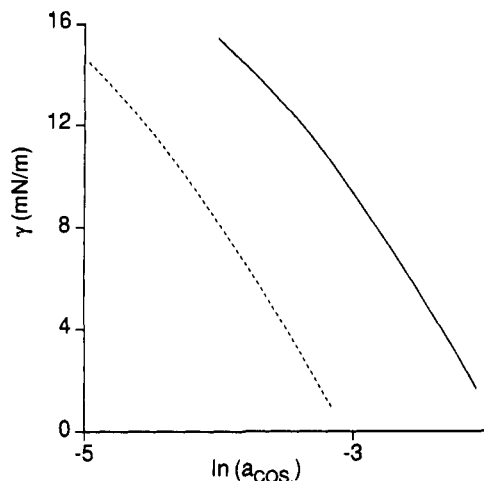


Figure 5. Interfacial tension between oil and water in the presence of SDS, salt, and pentanol (solid line) or hexanol (dashed line) as a function of the logarithm of the cosurfactant activity (mol/L).

Table IV. Parameter Values for Cosurfactant Interfacial Excess Concentration According to Equations 2 and 3

	pentanol	hexanol
$\Gamma_{co,\infty}$ ($\mu\text{mol}/\text{m}^2$)	4.44 ± 0.06	4.46 ± 0.10
A (mol/m^3)	24.72 ± 0.81	7.80 ± 0.29

Table V. Cosurfactant Interfacial Excess Concentrations (Γ_{co} , $\mu\text{mol}/\text{m}^2$), Adsorption Ratios (Γ_{co}/Γ_{SDS} , mol/mol), Total Interfacial Excess Concentrations ($\Gamma_{co} + \Gamma_{SDS}$, $\mu\text{mol}/\text{m}^2$) and Mean Molecular Areas (σ_{mean} , nm^2)^a

x°_{init}	Γ_{co}	Γ_{co}/Γ_{SDS}	$\Gamma_{co} + \Gamma_{SDS}$	σ_{mean}
Pentanol				
0.00	0.00	0.00	3.62	0.46
0.01	2.85 ± 0.09	1.12	5.39	0.31
0.02	3.26 ± 0.13	1.55	5.36	0.31
0.05	3.55 ± 0.15	1.77	5.56	0.30
0.10	3.64 ± 0.15	2.01	5.45	0.30
0.20	3.73 ± 0.15	2.12	5.49	0.30
1.00	4.7		4.7	0.35
Hexanol				
0.00	0.00	0.00	3.62	0.46
0.01	2.62 ± 0.16	0.97	5.32	0.31
0.03	3.15 ± 0.19	1.45	5.32	0.31
0.05	3.30 ± 0.20	1.82	5.11	0.32
0.075	3.38 ± 0.20	1.83	5.23	0.31
0.10	3.40 ± 0.20	1.83	5.26	0.31
0.20	3.51 ± 0.21	2.05	5.22	0.32
1.00	4.7		4.7	0.35

^a Γ_{lin}^{SDS} from Table I was used.

For the highest SDS concentrations at which no cmc is exceeded, values for $\Gamma_{co,\infty}$ and A in (2) are presented in Table IV. From (2) and Table IV we deduce that at initial weight fractions cosurfactant higher than about 0.05 (corresponding to a pentanol activity of 9.20×10^{-2} mol/L and a hexanol activity of 2.16×10^{-2} mol/L in the water phase) the cosurfactant interfacial concentration does not increase significantly although its saturation value as obtained from the Szyszkowski equation (2) is markedly higher. Table V gives some values of the cosurfactant interfacial concentration obtained from (2) and Table IV and a comparison of the adsorption ratios and packing densities of the two cosurfactants.

From these results it follows that the molecular composition of the interface is independent of the cosurfactant used and the behavior of the interfacial composition as a function of the cosurfactant concentration is highly comparable: at low cosurfactant concentrations (initial

weight fraction <0.05) a strong pushing out effect is observed, i.e. the area per SDS molecule increases dramatically from 0.46 nm^2 to about 1 nm^2 . At higher concentrations, the composition of the interface remains nearly constant and a high packing density of the mixed monolayer compared to single component adsorptions is observed.

Discussion and Conclusion

In this work, one of the questions we addressed is whether or not the composition of the interface changes if two slightly different cosurfactants are used. The answer appears to be very simple: it does not change significantly so the difference in phase behavior of the microemulsion systems observed must be due to a more subtle effect than just a difference in surface composition. A discussion in terms of differences in the values of the bending elastic moduli and natural radii of the interface is presented in ref 5.

It is proved that the approximation of saturation adsorption in the vicinity of the cmc gives rise to comparable interfacial concentrations to those obtained by the application of the Szyszkowski equation over a broader range. From the application of the Szyszkowski equation, it is however found that the SDS interfacial concentrations do not significantly differ from their saturation values but the cosurfactant interfacial concentrations definitely do. Even at the highest cosurfactant concentrations, the saturation value is significantly higher than the interfacial concentration close to the cmc.

The constancy of the interfacial composition as a function of the cosurfactant concentration is not in agreement with observations in other systems. Zhou and Dupeyrat⁸ find, using lower cosurfactant concentrations (butanol, pentanol, and benzyl alcohol up to 0.10 (w/w)) and a rather high salt concentration (0.43 M), a strong competition effect over the whole range of cosurfactant concentrations in dodecane: in the pentanol system, the molecular area of SDS increases from 0.46 up to 1.8 nm^2 . As a consequence, a much higher cosurfactant/SDS ratio is found: $\Gamma_{co}/\Gamma_{SDS} = 4.9$. These results are qualitatively in agreement with calculations by Ruckenstein et al.²³ on systems in which the chain length of the linear alkane, the surfactant, and the cosurfactant are varied. Aveyard et al.⁷ find an even higher cosurfactant SDS ratio ($\Gamma_{co}/\Gamma_{SDS} = 5.5$) in a system containing octanol (up to 5% (w/w)), cyclohexane, and 0.3 M NaCl at 30°C . As pointed out in ref 16, the pentanol interfacial concentration used by Verhoeckx et al.⁶ is too high because of their assumption that the pentanol interfacial concentration in the mixed monolayer should be equal to its saturation adsorption value without SDS. This is in contradiction with (12) and the observation that Γ_{SDS} for mixed adsorption is different from the value without pentanol.

It is interesting to note that in all cases discussed above, the mean area per molecule in the mixed monolayer is constant and equals approximately 0.30 nm^2 , significantly lower than the values for single-component adsorption.

Acknowledgment. The authors are indebted to Jacques Suurmond for his contribution to the experimental work and to Tibor den Ouden for providing the fit procedure.

(23) Ruckenstein, E.; Rao, I. V., *J. Colloid Interface Sci.* 1987, 117, 104.