On Understanding Microemulsions

III. Phase Equilibria in Systems Composed of Water, Sodium Chloride, Cyclohexane, SDS, and *n*-Pentanol

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At low concentrations (<4.2%) of sodium dodecyl sulfate (SDS) in water we found the well-known transition from Winsor I (O/W + O) via Winsor III (W + microemulsion + O) to Winsor II (W/O + W) equilibria with increasing concentrations of salt and pentanol (the cosurfactant). Above 4.2% SDS the Winsor III region was replaced by a single-phase region, and at very high concentrations (10% and higher) liquid crystalline phases appeared. We carried out chemical analyses of the phases in equilibrium mostly in the Winsor II region at 0.3 M NaCl and measured interfacial tensions between microemulsions and excess water phases. The cosurfactant is distributed among oil, water, and the interface. Its activity in the oil and water regions together with the NaCl concentration determines the droplet size. The SDS goes nearly all to the interface. This is important for the volume fraction but not for the size of the droplets. The negative adsorption of the NaCl at the high surface charge density of the interfaces resulted, even at 0.3 M NaCl, in a significant increase of the NaCl concentration with a sizable influence on the droplet size. Droplet sizes agreed quite well with theoretical expectations over the ranges of cosurfactant activities and volume fractions investigated. Interfacial tensions changed with cosurfactant activities as expected, but increased somewhat with the volume fraction, whereas a small decrease was expected. Nevertheless the differences between theoretical and experimental values remain fairly small. © 1989 Academic Press, Inc.

INTRODUCTION

In our previous, mainly theoretical, paper (1) on the thermodynamics of droplet-type microemulsions we pointed out that the behavior of microemulsions depends on the bending stress in the interface and thus is affected strongly by the following:

—the electrolyte content of the water-rich medium, which controls the thickness of the electrical double layer and therefore influences the electrical contribution to the bending stress;

—the cosurfactant content of the oil-rich medium, which influences the adsorption of the cosurfactant and the surfactant. This affects the bending stress for two reasons. An increased bulk concentration of the cosurfactant causes a higher lateral pressure in the li-

pophilic chain region, thus promoting bending of the interface around the water side. It also causes a small, but significant, decrease of the surface excess concentration of the ionic surfactant, thus decreasing the bending effect of the double layer and again promoting the formation of water droplets in oil.

In this paper we report on a study of the phase equilibria of the system water, NaCl, cyclohexane, sodium dodecyl sulfate (SDS), and *n*-pentanol. Special attention will be paid to the effect of the concentrations of NaCl and of the surfactants on the solubilization of water, the droplet radii, and the interfacial tensions in the Winsor II region (W/O + O). The experimental results will be compared with theoretical predictions (1).

Nearly all the surfactant (except for the small (<CMC) equilibrium concentration)

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and a considerable fraction of the cosurfactant are present in the interface. The rest of the cosurfactant is distributed between the water-rich and the oil-rich regions. Initial cosurfactant concentrations must therefore be corrected for adsorption and distribution in order to obtain free cosurfactant concentrations (or activities) in the continuous medium. NaCl is not present in the oil-rich medium, but the initial salt concentration must be corrected for the *negative adsorption* at the charged interface of the droplets.

The necessary data for the correction of the cosurfactant concentration were presented earlier (2). The negative adsorption of NaCl is obtained from double-layer theory and also from measurements of the increase in NaCl concentration in the equilibrium water phase compared to those of the initial salt concentration.

EXPERIMENTAL

Eight (8.00) grams of a mixture of cyclohexane and pentanol were added to 10.00 g of an aqueous solution of NaCl and SDS. The oil contained up to 28% (w/w) pentanol. The aqueous mixtures were solutions of 0.10, 0.20, 0.30, or 0.40 M NaCl in water, that also contained 0.04–15% (w/w) SDS. Spontaneous emulsification usually occurred upon adding the oil phase to the water phase. Equilibration in glass tubes with Teflon-sealed screw caps was promoted by gently swirling around the two- or three-phase systems, thereby avoiding gross emulsification. After equilibration for at least 1 month at 25°C, the samples were allowed to rest 1 week before further analyses and measurements were made.

The origin and quality of the materials and most experimental techniques have been discussed in Ref. (2). Here we describe only a few adaptations and new techniques.

Since a considerable amount of solubilization occurs, densities of the equilibrated phases of all samples were measured for the determination of interfacial tensions with the spinning drop technique. For these measurements

a Paar DMA 02C digital precision densitometer was used.

The chloride content of the excess aqueous phases in the Winsor II region was determined by potentiometric titration with silver nitrate. The water content of the coexisting W/O microemulsions was determined by gas chromatography, under conditions described in Ref. (2), with a thermal conductivity detector.

RESULTS AND DISCUSSION

Phase Equilibria

In our five-component system a great variety of phases occurs. We shall limit our treatment to the so-called Winsor I, Winsor II, and Winsor III equilibria (see Ref. (1), Fig. 1) in which microemulsions are in equilibrium with a surfactant-lean oil phase, or a surfactant-lean water phase, or with both.

In Fig. 1 we show the influence of salt and of cosurfactant on the type of equilibrium obtained at a fixed low SDS concentration of 1% (w/w), if we start off at nearly equal volumes of an aqueous phase (10 g) and an oil phase (8 g) at 25°C. Note that all compositions given refer to initial concentrations, unless mentioned otherwise. At low cosurfactant and
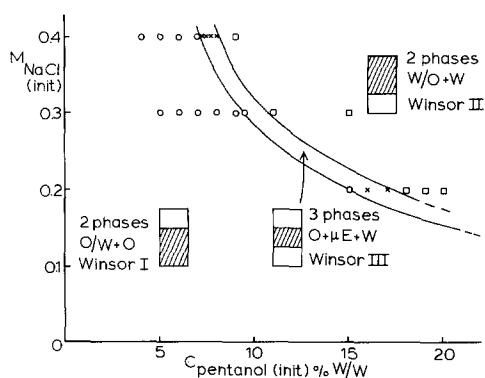

FIG. 1. Different types of phase equilibria after equilibration of 8 g of a solution of pentanol in cyclohexane (pentanol concentration on the horizontal axis) and 10 g of a solution 1% (w/w) SDS in brine (NaCl concentration on the vertical axis). The curves represent the boundaries between Winsor I/Winsor III and Winsor III/Winsor II equilibria as used in Table III of Ref. (1). O, Winsor I; ×, Winsor III; □, Winsor II; μE, middle phase microemulsion.

electrolyte contents Winsor I (O/W + O) equilibria are found, at high cosurfactant and electrolyte contents the equilibria are Winsor II (W/O + W), and in between there is a narrow band of Winsor III equilibria (microemulsion + O + W). In general, on approaching the three-phase region from either two-phase region, the phase volume of the microemulsion and its turbidity are observed to increase.

We did a few experiments with n-heptanol instead of n-pentanol as the cosurfactant. The transition from Winsor I to Winsor II equilibria (via a very turbid narrow (W III?) transition region) is shifted by 5% and more to lower cosurfactant concentrations and Winsor II equilibria occur even below 0.1 M NaCl. In accordance with the model used in Ref. (1) the longer chain of the cosurfactant gives a stronger negative contribution to the bending stress coefficient c and promotes W/O-type curvature of the interface.

More detailed experiments with n-pentanol were carried out at 0.3 M NaCl. Figure 2 shows how the three-phase region shifts to higher cosurfactant concentrations when the ionic surfactant concentration increases. This is mainly due to the adsorption of the cosurfactant at the interface between oil and water, as can be concluded from the following argument. We
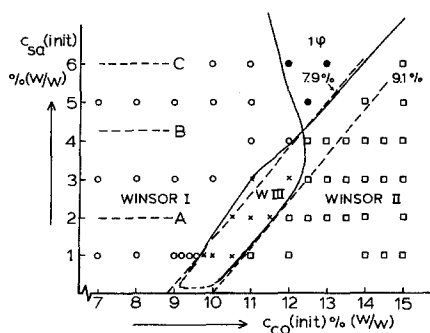
have inserted two dotted lines corresponding to 7.9 and 9.1% (w/w) cosurfactant in the oil-rich regions in Fig. 2. These lines have been calculated on the following basis:

(i) The concentration of pentanol in the aqueous regions is close to 0.8% (w/w) for the given concentrations (7.9–9.1%) in cyclohexane, as found from the pentanol distribution data in Ref. (2).

(ii) The molar ratio of pentanol to SDS in the interface is about 2.4 according to interfacial tension data in Ref. (2).

(iii) Virtually all SDS is in the interface.

At least for the lower SDS concentrations the dotted lines follow the Winsor I/Winsor III (volume of water phase is zero) and the Winsor III/Winsor II (volume of oil phase is zero) boundaries rather closely, indicating that these boundaries are controlled by the pentanol activity and not by its concentration. Straight lines corresponding to constant pentanol activity for these boundaries will also be found according to the pseudo phase model for microemulsions proposed by Biais *et al.* (3). We shall discuss later why the Winsor I/Winsor III boundary continues straight to higher surfactant concentrations but the Winsor III/Winsor II boundary curves to the left.

At very low SDS content we have not explored the phase behavior in detail. In Fig. 2 we have closed the three-phase region at the lower end by a dotted line at an SDS concentration of about 0.1%, since there is no three-phase region in the absence of SDS and we have observed at 0.1% the appearance of a middle phase. We have not explored the phase behavior between 0 and 0.1% SDS in any detail.

In all three multiphase regions in Fig. 2 the volume of the surfactant-rich phase (the microemulsion) increases with SDS addition, until at high-surfactant concentration a one-phase region is entered. Figure 3 shows this effect schematically for a sequence of surfactant concentrations (indicated by A, B, and C in Figs. 2 and 3).

FIG. 2. Phase behavior with 0.3 M NaCl as a function of the SDS concentration in the aqueous phase and the pentanol concentration in the oil phase. O, Winsor I; ×, Winsor III; □, Winsor II. The solid curves give the approximate boundaries between the different multiphase regions. The broken lines are calculated to have constant pentanol concentration in the oil-rich medium.
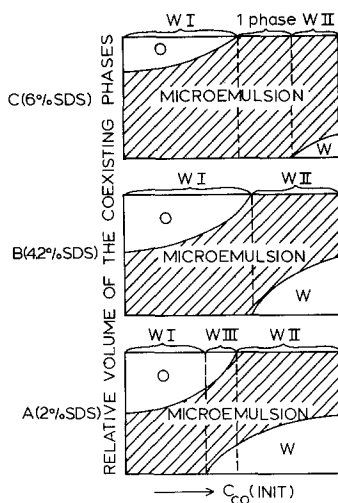
FIG. 3. Schematic representation of the relative volumes of the coexisting phases for three cross sections (A, B, and C) through Fig. 2 at different surfactant concentrations. The Winsor types of phase equilibrium are indicated above each diagram. The figure illustrates that a continuous transition from O/W to W/O microemulsions exists.

The cross-hatched microemulsion region expands upon addition of surfactant, or stated differently, the regions O and W withdraw because the solubilizing capacity of the microemulsion increases. From Fig. 3 we note that a direct transition from a three-phase region to a single-phase region, as suggested by the intersecting boundaries of the three-phase region at level "B" in Fig. 2, is indeed possible. Furthermore it becomes clear that there is only one microemulsion region. Within this region a continuous transition is possible from an O/W to a W/O droplet-type microemulsion, without passing through a multiphase region. It is highly probable that such a transition takes place via *bicontinuous microemulsions* (4, 5). In these systems regions of oil and of water are interdispersed and their boundaries may fluctuate in time. Also, both oil and water regions extend continuously throughout the microemulsion.

This does not imply of course that the boundaries between droplet-type microemulsions and bicontinuous microemulsions coincide with the boundaries of the three-phase region.

First, even in droplet-type microemulsions the equilibrium is dynamic. Droplets form and disappear continually; their shape may fluctuate and this will lead to some degree of local bicontinuity. Bicontinuous structures may therefore already exist in the two-phase regions, especially close to the three-phase boundary.

Second, several authors (6–8) have suggested that a droplet-type microemulsion can disproportionate into a concentrated and a (very) dilute microemulsion of the same type (W/O or O/W). As in the case of liquid–gas equilibria attractive forces between the droplets are responsible for this phenomenon. Far from the critical point the more dilute of the two microemulsions closely resembles a droplet-free continuous medium. This implies that the possibility of droplet-type microemulsions as the middle phase in the Winsor III region cannot be excluded.

High Concentrations of SDS

When the initial concentration of SDS is increased above 10% (w/w), the single-phase region (1ϕ of Fig. 2) divides into three different single-phase regions separated by two zones of two-phase equilibria. Preliminary results of small-angle X-ray scattering (SAXS) suggest a liquid crystalline structure for the central single-phase region, but its exact structure could not be determined unambiguously.

The main conclusion from these observations is that, at high-surfactant concentrations, the transition from O/W microemulsions to W/O microemulsions by increasing the cosurfactant concentration is not continuous via random structures, but discontinuous via ordered structures.

The Winsor II Region

We have investigated the phase equilibria W/O + W in more detail, because our theoretical treatment (1) focused especially on W/O systems. For 0.3 M NaCl (initial) and initial pentanol concentrations from 11 to 28% (w/w), we have determined the compositions of

the coexisting W/O microemulsions and aqueous phases.

Figure 4 gives the amount of water solubilized in the microemulsions versus the total amount of SDS in the system at a number of initial concentrations of pentanol in cyclohexane. The water content is seen to increase with increasing amounts of SDS and with decreasing amounts of cosurfactant. As under all conditions in Fig. 4, SDS is adsorbed to saturation (see (2)); more SDS results in more interfacial area, A_d. At constant concentrations of salt and cosurfactant the preferred curvature of the interface is constant and, except for a modest influence of the amount of water solubilized, the droplet radius, a, is constant (1), and thus according to Eq. [1] the amount solubilized should increase linearly with the amount of SDS,

$$a = \frac{3 \times 4/3\pi a^3}{4\pi a^2} = \frac{3V_d}{A_d}, \qquad [1]$$

where V_d is the total volume of the droplets.

It is evident from Fig. 4 that the amount of water m_w increases more than linearly with m_{SDS}. This is mainly due to the fact that with more interface proportionally more pentanol adsorbs. Along the lines of constant initial concentrations of pentanol the actual concentration in the continuous medium therefore decreases with increasing amounts of SDS.
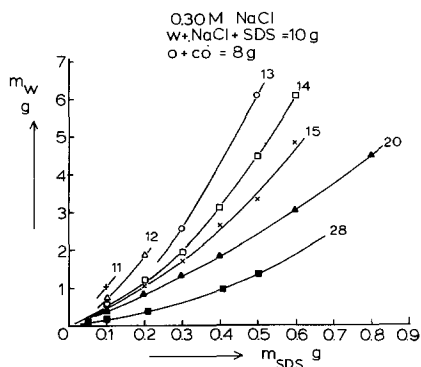

FIG. 4. Solubilization of water in the Winsor II region plotted against the amount of SDS. The numbers and the different symbols represent samples with different initial pentanol concentrations (in %, w/w) in the oil phase.

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TABLE I

W/O Microemulsions Coexisting With Excess Aqueous Phase, Formed from 10 g Aqueous Solution, 0.3 M in NaCl with C_{SDS} (%, w/w), and 8 g Cyclohexane Containing C_{co} (%, w/w) Pentanol[a]

C_{co} (init.) (%, w/w)	C_{SDS} (init.) (%, w/w)	m_w (g)	$C_{co,cm}$ (%, w/w)	a (Å)	φ
11	1	1.057	9.18	174	0.112
12	1	0.730	10.17	120	0.085
12	2	1.828	9.32	151	0.184
13	3	2.54	9.49	140	0.242
13	5	6.07	7.79	203	0.426
13.5	2	1.412	10.82	115	0.154
13.5	3	2.16	9.98	118	0.219
13.5	4	3.86	9.14	159	0.325
14	1	0.580	12.16	94	0.072
14	2	1.186	11.33	97	0.137
14	3	1.933	10.49	105	0.204
14	4	3.12	9.64	128	0.287
14	5	4.48	8.78	148	0.363
14	6	6.06	7.95	168	0.433
14.5	1	0.552	12.67	89	0.069
14.5	3	1.799	10.99	98	0.195
14.5	4	2.83	10.14	116	0.271
15	1	0.478	13.17	77	0.062
15	2	1.074	12.33	87	0.128
15	3	1.692	11.50	92	0.187
15	4	2.60	10.65	106	0.258
15	5	3.32	9.79	109	0.308
15	6	4.83	8.94	133	0.387
20	1	0.393	18.20	62	0.055
20	2	0.834	17.39	66	0.109
20	3	1.320	16.58	70	0.161
20	4	1.824	15.76	73	0.210
20	6	3.04	14.06	81	0.305
20	8	4.51	12.33	91	0.393
20	10	6.37	10.60	104	0.476
28	0.4	0.089	26.76	35?	0.016
28	1	0.177	26.32	28	0.034
28	2	0.402	25.58	31	0.071[5]
28	4	0.986	24.05	39	0.150
28	5	1.359	23.26	43	0.192
28	10.4	3.36	18.80	51	0.368
28	15	5.22	14.72	56	0.480[5]

[a] m_w is the observed mass of water in the microemulsion at equilibrium, $c_{co,cm}$ is the calculated (see text) percentage (w/w) pentanol in the continuous medium of the microemulsion, a (Eq. [1]) is the radius, and φ (Eq. [3]) the volume fraction of the droplets.

This decrease of the pentanol concentration thus increases the preferred radius of curvature and so the droplet radius.

This is shown more quantitatively in Table I, which lists the observed amount of solubilized water, m_w, for various initial conditions. With these data the final concentration of pentanol in the continuous medium, $C_{co,cm}$, the radius, a, and the volume fraction, ϕ, of the droplets are determined in the following way.

Make a *first estimate* of $C_{co,cm}(I)$ by assuming that the concentration of pentanol in water $C_{co,w}$ is 0.9% (w/w) (cf. Fig. 7 of Ref. (2)) and the amount of pentanol in the interface is 2.47 moles for each mole of SDS in the system. This ratio corresponds to $\Gamma_{co} = 4.62 \times 10^{-6}$ mole m^{-2} (Ref. (2)) and $\Gamma_{SDS} = 1.87 \times 10^{-6}$ mole m^{-2} (average from Ref. (1, Table III)).

A refined estimate of $C_{co,cm}(II)$ is then made by finding better values for $C_{co,w}$ (Fig. 7 of Ref. (2)) and Γ_{SDS} (Ref. (1, Table III)) for

each value of $C_{co,cm}(I)$, and by calculating the amount of pentanol in the interface $g_{co,interf.}$ from

$$g_{co,interf.} = \Gamma_{co} \times A_d \times M_{co}$$
$$= \frac{4.62 \times 10^{-6} \text{ mole m}^{-2}}{\Gamma_{SDS}} \times \frac{88}{288} \times g_{SDS}, \quad [2]$$

where $M_{co} = 88$ is the molecular weight of pentanol and g_{SDS} is the total amount of SDS in the system, thus neglecting the small amount of SDS dissolved in the aqueous regions.

With A_d and V_d (from m_w and assuming that the salt concentration is 0.3 M in the aqueous regions) known, the droplet radius a is calculated from Eq. [1] and the volume fraction ϕ is found from Eq. [3] which is equivalent to Eq. [31] of Ref. (1),

$$\phi = \frac{\dfrac{m_w + m_{NaCl}}{1.0094 \text{ g cm}^{-3}} + \dfrac{g_{SDS}}{1.45 \text{ g cm}^{-3}} + \dfrac{g_{co,w}}{0.8 \text{ g cm}^{-3}}\dfrac{m_w + m_{NaCl}}{g_w + g_{NaCl}} + \dfrac{g_{co,interf.}}{0.8 \text{ g cm}^{-3}}}{\dfrac{m_W + m_{NaCl}}{1.0094 \text{ g cm}^{-3}} + \dfrac{g_{SDS}}{1.45 \text{ g cm}^{-3}} + \dfrac{g_{co,w}}{0.8 \text{ g cm}^{-3}}\dfrac{m_W + m_{NaCl}}{g_W + g_{NaCl}} + \dfrac{g_{co,interf.}}{0.8 \text{ g cm}^{-3}} + \dfrac{g_{cyclohex.} + g_{co,o}}{0.8 \text{ g cm}^{-3}}},$$
$$[3]$$

where m_W and m_{NaCl} are the amounts of water and NaCl, respectively, in the microemulsion, g_i is the amount of component i in the total system (10 g water + NaCl + SDS, 8 g cyclohexane + pentanol (=co)), and $g_{co,w}$, $g_{co,interf.}$, and $g_{co,o}$ are respectively the amounts of pentanol in the aqueous regions, the interface, and the oil regions.

Figure 5 gives a plot of the droplet radius versus the equilibrium concentration of pentanol. The radius is seen to increase more rapidly with decreasing pentanol concentration, when the three-phase region is approached. Contrary to theoretical expectations (Ref. (1)) no clear systematic effect of the volume fraction, ϕ, shows up. Only at the highest volume fractions is a tendency to a lower value of a observed. This near lack of influence of ϕ may

be due to the negative adsorption of NaCl which we shall now consider.

Negative Adsorption of NaCl

The high surface charge density of the droplet interfaces repels the Cl$^-$ ions (the co-ions), causes negative adsorption of NaCl, and thus leads to an increase of the bulk NaCl concentration. We checked this quantitatively by a theoretical calculation and by measuring the NaCl concentration in the excess aqueous phase.

The same effect has been described by Levine and Robinson (9) and more extensively by Biais *et al.* (10). Levine and Robinson calculate the negative adsorption using the Pois-
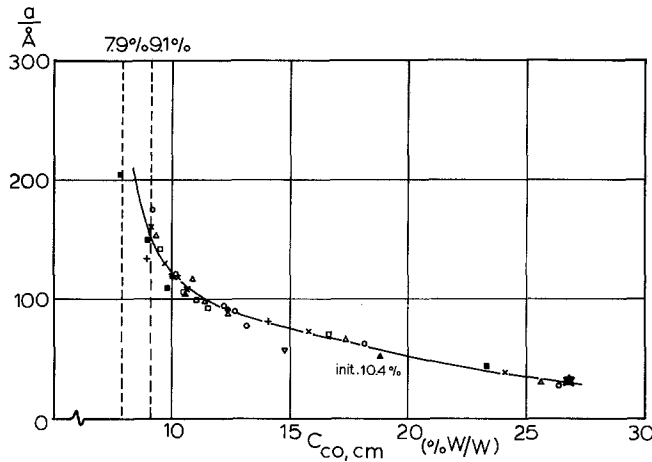
FIG. 5. Observed droplet radius vs the pentanol concentration, $C_{co,cm}$, in the continuous medium for W/ O microemulsions that coexist with an aqueous phase. See Table I and text. The different symbols ($\star$, O, $\triangle$, $\square$, $\times$, $\blacksquare$, +, $\bullet$, $\blacktriangle$, $\triangledown$) correspond to initial SDS concentrations of 0.4, 1, 2, 3, 4, 5, 6, 8, 10, and 15% (w/ w), respectively. The vertical broken lines correspond with those in Fig. 2. The drawn curve serves as a guide for the eye.

son–Boltzmann equation and report their results as the ratio of the average concentration in the droplets to that in the outside phase.
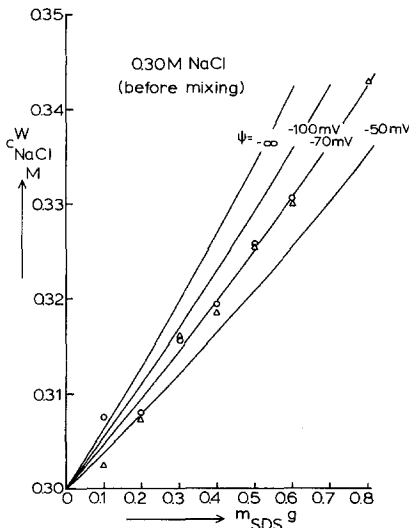

FIG. 6. Equilibrium concentration of NaCl in the excess aqueous phase versus the amount of surfactant in the microemulsion at initial pentanol concentrations of 14% (O) and 20% (w/w) ($\triangle$) in cyclohexane. The curves are calculated from double-layer theory for different surface potentials (ψ_0 in Eq. [4]).

They give a limited number of numerical results and hardly any comparison with experiments. Biais et al. treat the electrolyte equilibrium between droplets and bulk aqueous phase as a Donnan equilibrium assuming a constant concentration of ions throughout the droplet. They give a fairly extensive list of experimental results and bring their theory and experiments into agreement by assuming some hydration of the polar groups and a finite dissociation constant for SDS.

Our experimental results are given in Fig. 6 for two different initial concentrations of pentanol (14 and 20%). This figure also includes curves of theoretical calculations based on double-layer theory for a few selected surface potentials. It is clear that especially for the higher amounts of SDS the bulk NaCl concentration is significantly increased.

For a flat electrical double layer use of the complete nonlinearized Poisson–Boltzmann equation leads to a negative adsorption of co-ions equal to

$$\Gamma_{Cl} = -C_{NaCl}(2/\kappa)(1 - \exp(F\psi_0/2RT)),$$

$$[4]$$

where $\kappa^2 = 2C_{NaCl}F^2/\epsilon_r\epsilon_0 RT$ and C_{NaCl} is the concentration far from the interface. ψ_0 (negative) is the surface potential, F the Faraday constant, ϵ_r the dielectric constant of the aqueous solution, ϵ_0 the permittivity of the vacuum, R the gas constant, and T the absolute temperature.

The use of Eq. [4], strictly valid only for a flat double layer, is justified; since $1/\kappa$ for 0.3 M NaCl is only 5.55 Å, more than 95% of the negative adsorption occurs within $3/\kappa$ from the surface, and the particle radii are (in the cases considered) larger than $10/\kappa$.

From our theoretical analysis (1) of the Winsor II equilibrium we know that the equilibrium salt concentration is the same in the droplets and in the excess aqueous phase. This concentration (C_{NaCl} in Eq. [4]) can therefore be found from the expression

$$C_{NaCl,init.} \times V_w = C_{NaCl} \times V_w + \Gamma_{Cl}A_d \quad [5]$$

and A_d is proportional to the amount of SDS as in Eq. [2]. In Fig. 6 curves of C_{NaCl} are shown for a few chosen values of ψ_0. A surface potential of $\psi_0 = -70$ mV fits the data rather well. The surface charge density, σ_{CH}, corresponding to this potential is found from

$$\sigma_{CH} = \epsilon_r\epsilon_0\kappa(2RT/F)\sinh(F\psi_0/2RT). \quad [6]$$

It leads to $\sigma_{CH} = -0.12$ C m^{-2}, which is about two-thirds of the charge density corresponding to $\Gamma_{SDS} = 1.87 \times 10^{-6}$ mole m^{-2}, assuming complete dissociation. As far as comparison is possible our experimental results agree well with those of Biais *et al.* (10) and the two theoretical interpretations give about the same kind of agreement with the experiments. In a later publication we shall present more data on the salt exclusion which is only of secondary concern in this paper.

We conclude that the increase found in the NaCl concentration is explained well by the negative adsorption at the highly charged interface. Before considering the influence of this change in NaCl concentration on the phase equilibria we give a brief recapitulation of the most important results of Ref. (1).

Recapitulation of the Theory on Phase Equilibria (1)

For the Gibbs free energy, G^M, of the microemulsion we derived the expressions (Ref. (1, Eqs. [20] and [25]))

$$G^M = \sum n_i\mu_i = \sum n_i\lambda_i + n_d \frac{4\pi a^2}{3}$$
$$\times \left[\sigma + 2\frac{c}{a} + \frac{3kT}{4\pi a^2}f(\phi, a)\right] \quad [7]$$

with

$$f(\phi, a) = \ln\phi - 1$$
$$+ \phi\frac{4 - 3\phi}{(1 - \phi)^2} - \frac{3}{2}\ln\frac{16a^3}{v_w}. \quad [8]$$

In these equations n_i and μ_i are the amount and the chemical potential, respectively, of component i (i = water, NaCl, SDS, cyclohexane, pentanol). λ_i is the chemical potential of component i when the droplets are considered to be fixed in the laboratory coordinates. n_d, a, and ϕ are the number, radius, and volume fraction, respectively, of the droplets; σ is the interfacial tension of the droplets; $c = [\partial\sigma/\partial(2/a)]_{T,p,\lambda_i}$ is the bending stress coefficient of the interface; k is the Boltzmann constant; and v_w is the molecular volume of water.

The internal equilibrium in the microemulsion requires dG^M (all n_i constant) = 0 and leads to

$$\sigma + \frac{2c}{a} + \frac{3kT}{4\pi a^2}f(\phi, a)$$
$$= -\frac{3kT}{4\pi a^2(1 + 2x/a)}$$
$$\times \left(\frac{y\phi g(\phi)}{(a + 3(x + y))} + \frac{3(a + 3x)}{2a}\right), \quad [9]$$

where

$$g(\phi) = \partial f(\varphi, a)/\partial\phi$$
$$= (1 + \varphi + \varphi^2 - \varphi^3)/\phi(1 - \varphi)^3 \quad [10]$$

and

$$x = \Gamma_{SDS} V_{SDS} + \Gamma_{Cl} V_{NaCl} \quad \text{and} \quad y = \Gamma_{co} V_{co}$$
[11]

with V_i as the molar volume of component i.

External equilibrium of the microemulsion with excess aqueous phase requires that

μ_i (microemulsion)

$$= \mu_i \text{ (excess aqueous phase)} \quad [12]$$

for i = water, NaCl, and SDS (the influence of the small solubility of pentanol and cyclohexane in water has been neglected). This requirement leads to a second relation (Eq. [48] of Ref. (1)) between σ and c with the compositional parameters of the emulsion, and from the two relations σ and c are found separately. The relation for c is

$$c = \frac{kT}{4\pi a}\left[-f(\varphi, a)\right.$$

$$\left. + \frac{a\varphi g(\varphi)}{2(a + 3(x + y))}(1 - \varphi) - \frac{9}{4}\right]. \quad [13]$$

The bending stress coefficient, c, can also be found from model considerations, using the curvature dependence of the free energy of the electrical double layer, and that of the rather tightly packed hydrocarbon tails of the surfactants,

$$c = c_{el} + c_{tails} = A + B/\kappa a - D \exp(-l/a), \quad [14]$$

where A and B are known functions of the surface charge density, σ_{CH}, the Debye length $1/\kappa$, and ξ. As treated in more detail in Ref. (1), the parameter ξ denotes a (small) distance separating the radius a of the equivalent water sphere ($\Gamma_{H_2O} = 0$) of the droplet and the radius $(a + \xi)$ where (for saturation adsorption) the surface concentration of surfactant and cosurfactant stays constant on bending. The length l is of the order of the length of the hydrocarbon tails of the surfactant and cosurfactant. It depends strongly on the choice of ξ (see Ref. (1, Table II)). D is of the order of 7

$\times 10^{-12} N$. It varies somewhat with ξ and very slightly with the cosurfactant concentration. (See Ref. (1, Tables II and III).)

For given conditions (temperature, electrolyte concentration, volume fraction) the particle radius, a, and c can be calculated from Eqs. [13] and [14].

The interfacial tension, σ, is not easily accessible, but the closely related interfacial tension, γ_{MW}, between a microemulsion and a coexistent aqueous phase can be measured and can also be derived theoretically (Ref. (1, Eq. [79])).

In Ref. (1) we showed that for a low volume fraction ($\varphi = 0.05$) the agreement between theory and experiments was excellent for the radii and acceptable for the interfacial tensions. We shall now look more closely at higher volume fractions, i.e., at higher initial concentrations of SDS.

Comparison of Theory and Experiments at High-Volume Fractions, φ

In Ref. (1) we compared theoretical and experimental values of a and of γ_{MW} for two chosen values of ξ, viz. $\xi = 0.3$ nm and $\xi = 0.4$ nm with corresponding values of D and l (see Eq. [14]) for a low volume fraction, $\varphi = 0.05$. For these same parameters Fig. 7 shows how calculated values of a depend on the amount of SDS at constant equilibrium concentrations of NaCl (0.3 M) and of pentanol (19% (w/w)). a increases with m_{SDS}, as expected, since $\varphi/(1 - \varphi)$ increases nearly proportionally with m_{SDS}. But, as already mentioned in discussing Fig. 5, no clear systematic influence of m_{SDS} is found in experiments done with constant initial concentrations of NaCl. Due to the negative adsorption of NaCl its concentration increases with m_{SDS} and this effect leads to a decrease of a. The dotted lines in Fig. 7 demonstrate that the effect of φ (or m_{SDS}) on a becomes very small in the range considered (c_{SDS} 1–8%) but should show up at lower volume fractions, where, unfortunately, we do not have experimental data.
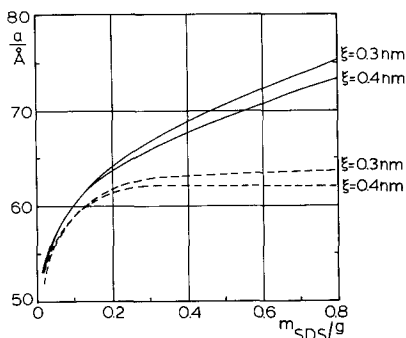
FIG. 7. Calculated droplets radii against the amount of SDS in Winsor II equilibria at an equilibrium concentration of 19% (w/w) pentanol in cyclohexane. (—) Equilibrium concentration of 0.3 M NaCl; (---) initial concentration of 0.3 M NaCl and negative adsorption taken into account.

Figure 7 confirms that ξ = 0.3 nm and ξ = 0.4 nm are good choices and that negative adsorption of NaCl should be taken into account.

It is now interesting to return to Fig. 2. At low concentrations of SDS the dotted lines for equilibrium concentrations of pentanol of 7.9 and 9.1% follow the boundaries WI/WIII and WIII/WII rather closely. At higher SDS con-
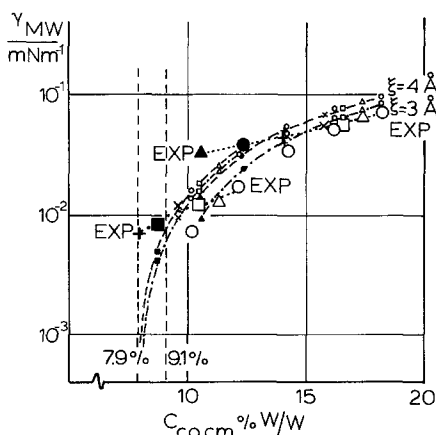

FIG. 8. Observed and calculated interfacial tensions, γ_{MW}, between W/O microemulsions and their excess aqueous phases. Symbols as in Fig. 5. Large symbols, measured; small symbols, calculated for ξ = 0.3 nm and ξ = 0.4 nm. See Fig. 5 for explanation of symbols.
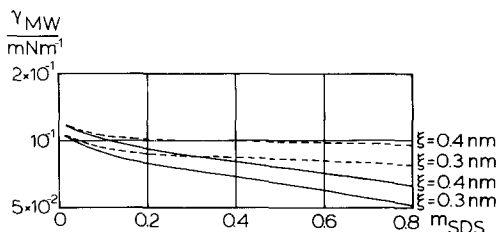

FIG. 9. Calculated interfacial tensions, γ_{MW}, for 0.3 M NaCl (initial) and 19% (w/w) final pentanol concentration. Solid lines, negative adsorption of NaCl neglected; dashed lines, negative adsorption of NaCl taken into account.

centrations the 7.9% line continues to follow the WI/WIII boundary and above 4.2% SDS the boundary between WII and the single-phase region. So this line may be considered the line where free water disappears or where a_{water} becomes large. At a constant concentration of pentanol a depends on m_{SDS} for two reasons: φ increases with m_{SDS} and a increases with φ as evident from Figs. 8 and 9 of Ref. (1) and from Fig. 7 above, but a decreases with increasing SDS due to negative adsorption of NaCl. For intermediate amounts of SDS the two effects compensate one another and the 7.9% line corresponds to very high radii ($a_{water} \rightarrow \infty$). At high amounts of SDS the negative adsorption effect predominates, and the radii become smaller (but remain still large) so that the 7.9% line can represent situations where 50% (by volume) of water is solubilized in the microemulsion irrespective of the amount of SDS.

The WIII/WII boundary and especially the WI/single-phase boundary, where free oil disappears, bend to the left with the increase of SDS. Here, in the O/W microemulsions with the electric double layer at the outside of the drops the two effects reinforce one another; a still increases with φ, but now the higher electrolyte concentration caused by negative adsorption of NaCl makes a_{oil} larger or allows a lower concentration of pentanol to keep the same amount of oil solubilized in the microemulsion.

The double-layer repulsion between pairs of particles acts in the same direction, but at 0.3 M NaCl the double-layer thickness and the range of the repulsion are too small to explain the curvature of the boundaries where oil disappears quantitatively.

Finally we come to the interfacial tensions, γ_{MW}, between W/O microemulsions and their excess aqueous phases. In Figs. 10 and 11 of Ref. (1) we showed that γ_{MW} could be calculated theoretically and that it showed the correct trend with variation of the NaCl and pentanol concentrations. The calculated values were somewhat high for 0.3 M NaCl, $\varphi = 0.05$ and equilibrium pentanol concentrations varying from 10–19% (w/w).

In Fig. 8 we now show all measured γ_{MW}'s for compositions given in Table I with c_{SDS} (init.) used as a parameter. One percent of SDS (init.) corresponds to about $\varphi = 0.09$ for c_{co} (init.) = 12% and $\varphi = 0.054$ for c_{co} (init.) = 20%. The data for higher SDS concentrations are taken from the two series with initial concentrations of pentanol of 14 and 20%. The results show that γ_{MW} at constant equilibrium concentrations of pentanol increases with m_{SDS} (and thus with φ). This is contrary to theoretical expectations as shown in Fig. 9 where values of γ_{MW} calculated with Eq. [79] of Ref. (1) and taking negative adsorption of NaCl into account are plotted against m_{SDS}.

To obtain another comparison between theory and experiments we calculated γ_{MW} with Eq. [79] of Ref. (1) for all experimental situations collected in Fig. 8 and inserted the results in that figure. Theoretical and experimental values move closer together for higher initial concentrations of SDS and actually become identical at C_{SDS} (init.) = 4–6% ($\varphi \sim 0.3$).

This agreement is gratifying if one considers that the calculations were done by using as calibration no interfacial tensions but only a few values of surfactant and cosurfactant adsorption, and the circumstances in which the radii go to infinity (see Ref. (1)). However, the opposite trends in γ_{MW} with φ for theory

and experiments show that there is still something missing in our understanding of this type of microemulsion.

CONCLUSIONS

The phase behavior of the microemulsion system studied here is typical for systems with a single-chain ionic surfactant and a medium-chain-length alcohol as the cosurfactant.

At constant salt concentration the boundaries between the Winsor I and Winsor III regions and between the Winsor III and Winsor II regions are mainly governed by the *activity of the cosurfactant* (its concentration in the water regions) and are practically independent of the amounts of surfactant and adsorbed cosurfactant.

In the Winsor II (W/O + W) region the NaCl concentration in the excess water phase increases with the amount of ionic surfactant in the system in good agreement with the theoretical expectation that the *NaCl activity* (its concentration far away from interfaces) is the same in the excess water and in the droplets, and that the high surface charge density leads to a sizable negative adsorption of the salt.

In the Winsor II region at constant activity of the cosurfactant the amount of water solubilized is proportional to the amount of ionic surfactant available and the droplet size is independent of it. This independence is due to a more or less accidental compensation of two effects. An increase of the volume fraction of droplets (at constant activities of salt and cosurfactant) leads to an increase of the droplet size but the increase of the salt concentration due to negative adsorption results in a decrease of the droplet size. At an initial salt concentration of 0.3 M and for not too small volume fractions, the two effects just compensate one another. Further experiments at other, particularly lower, salt concentrations and at low volume fractions, where the effect of φ on a should predominate, are desirable.

The measured interfacial tension, γ_{MW}, increases somewhat with the volume fraction of

droplets whereas the theoretical expectation is a decrease. The two effects are small and result in an equality of measured and calculated values at a volume fraction of about 0.3 or an initial surfactant concentration of about 4 to 6%.

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