Partitioning of Salt in Winsor II Microemulsion Systems with an Anionic Surfactant and the Consequences for the Phase Behavior

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The distribution of salt between the microemulsion phase and the excess aqueous phase for Winsor II type equilibria is studied experimentally. It has been observed that the salt concentration in the excess phase is significantly higher than the salt concentration in the initial aqueous phase before mixing with the oil phase. This implies that the average salt concentration in the water-rich regions of the microemulsion is smaller than the salt concentration in the excess phase. Under certain conditions the dispersed aqueous region is essentially salt-free. This highly unequal distribution of salt is due to the negative adsorption of co-ions. It can be quantitatively explained with the Gouy–Chapman–Stern theory adapted for spherical electrical double layers. Because of this unequal distribution of salt the initial solution of salt in water may not be regarded as a pseudocomponent of the system. The consequences of this phenomenon for the phase behavior of microemulsion systems are discussed, and in fact these appear to be of major importance to the ultimate interpretation of the phase behavior. © 1993 Academic Press, Inc.

1. INTRODUCTION

During the last two decades the solubilization of solutes (e.g., small ions, amino acids, and biopolymers) in microemulsion phases, and the partitioning of these solutes between a microemulsion phase and equilibrium phases, have received considerable attention. Especially the possibility of the application of reversed micellar solutions for the solubilization of proteins in apolar phases (1, 2), protein recovery by reversed micellar extraction (3, 4), and the use of the interior of reversed micelles as a reaction medium for chemical (often enzymatic) reactions (5, 6) explain the growing interest in these phenomena. The term reversed micellar solution is synonymous with W/O microemulsion, and the corresponding monophasic region in the phase diagram is the L_2 phase.

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Also salt (NaCl in this study), which is often present in microemulsion systems with an ionic surfactant, partitions between the microemulsion phase and the external aqueous phase of Winsor II systems (biphasic equilibrium between an L_2 phase and an aqueous phase) and Winsor III systems (triphasic equilibrium between an L_2 phase, an aqueous phase, and an oil phase). In this connection we note that several authors (7–14) have observed that in these systems the salt concentration of the brine dispersed in the microemulsion phase is significantly lower than in the external water rich-phase (referred to as "excess brine" in the remainder of the paper). This expulsion of salt into the external phase is usually explained on the basis of negative adsorption of salt in the electrical double layer at the interface formed by the charged surfactant heads.

The implication of the partitioning of salt on the phase behavior of the microemulsion system becomes apparent if we realize that the equilibrium conditions of these systems are strongly dependent on the salt concentration in the excess brine (15). Although this complicating effect was recognized before (1, 8, 15), it is usually thought that the increase of the salt concentration in the excess brine remains small and therefore has a negligible influence on the phase equilibria. De Bruyn *et al.* (11), however, showed that the effect can be large enough to explain some deviations between their theoretical predictions and experimental observations of Winsor II phase behavior.

In this paper our main focus is to demonstrate that in many cases the increase of the salt concentration is not at all small, and therefore should be taken into account in studies of the phase diagram to avoid serious misinterpretations (16). We performed an experimental study of Winsor II microemulsion systems with sodium dodecylsulfate (SDS) as the surfactant, pentanol as the cosurfactant, and cyclohexane as the oil.

The organization of the paper is as follows. First we show that the magnitude of the increase of the salt concentration may become quite large if the amount of excess brine becomes small with respect to the amount of brine solubilized in the microemulsion phase. Second a detailed study of salt partitioning in Winsor II equilibria is reported and it is shown

that the results can successfully be analyzed on the basis of the Poisson–Boltzmann equation for the adsorption of ions in a spherical electrical double layer. Finally we discuss the impact of the unequal distribution of salt on the phase diagram.

2. MATERIALS AND METHODS

Materials. Sodium dodecyl sulfate (SDS) was "specially pure" grade purchased from BDH, and was used without further purification. Small traces of dodecyl alcohol are known to be present in SDS. In microemulsion systems dodecyl alcohol will dissolve in the oil phase and also adsorb in the large internal interface. The amount adsorbed will, however, be negligible compared to the amount of adsorbed surfactant.

Cyclohexane and n-pentanol "analyzed" grade (Baker) were used without further purification.

NaCl "analyzed" grade (Baker) was heated for one hour at 150°C.

Deionized water was triply distilled before use.

Winsor II microemulsion systems. Part of the experimental program involved the measurement of the increase in the salt concentration in the excess water phase of Winsor II equilibria. Winsor II systems were produced in two different ways, in order to study the partitioning of salt in systems with a large amount of excess brine and in systems with a very small amount of excess brine.

Winsor II systems with a large amount of excess brine. Measurements were performed on a series of samples with an equilibrium pentanol fraction in the oil phase of 0.20 (w/w) and salt concentrations in the water phase before mixing of 0.200, 0.500, 1.000, and 5.000 M. The SDS concentration was varied between 0 and 0.20 (w/w) ($\approx 0.9\ M$) in the brine used to prepare the microemulsion, with the exception of the series with an initial salt concentration of 0.200 M, where the highest SDS concentration in the brine was 0.08 (w/w) ($\approx 0.3\ M$). The solubility of NaCl is exceeded at salt concentrations somewhat higher than 5.000 M, and salt concentrations much lower than 0.20 M could not be used with pentanol as the cosurfactant, because Winsor III or Winsor I equilibria were then established. The SDS concentrations in the samples were often so high that the uptake of pentanol in the interface of the microemulsion droplets led to a significant decrease of the pentanol concentration in the oil-continuous phase. Since the pentanol concentration in the oil phase strongly influences the droplet size, we compensated approximately for this uptake of pentanol by an extra addition of 0.7 g pentanol per g SDS to the system (corresponding to 2.3 molecules of pentanol per molecule SDS). This additional amount of pentanol is an average value determined by dilution titration (17). This method will be described below.

The samples were prepared by mixing 8.00 g of initial oil phase and 10.00 g of initial water phase in 25-ml glass tubes with Teflon-sealed screw caps at an ambient temperature of 24.7 ± 0.2°C. Experience shows that in the preparation of microemulsion systems containing relatively large amounts of surfactant, nonequilibrium liquid crystalline phases are often formed that break down only very slowly. We succeeded in producing equilibrium Winsor II systems within 1 or 2 days by the following procedure. The SDS is first wetted by the mixture of pentanol and cyclohexane, and then the SDS is partially dispersed and partially dissolved by using an ultrasonic bath. Then the brine is added carefully to the bottom of the tube containing this mixture, preventing the phases from mixing at this stage. Afterwards the tubes are allowed to equilibrate on a roller-bench at very low rates of revolution (≈ 1 rev/min). The rolling increases the speed of the diffusion processes occurring at the oil/water interface, whereas shaking or vigorous tumbling promotes the formation of persistent nonequilibrium phases. Once the samples are close to equilibrium, the systems are stable and can be shaken to complete the equilibration. The establishment of equilibrium is assessed visually and by the reproducibility of the measurements over time intervals of 1 week or longer.

Winsor II systems with small amounts of excess brine and dilution titration. In the titration procedure as first described by Bowcott and Schulman (18), alternate additions of cosurfactant and oil make the system move along the phase boundary between L_2 (W/O) and Winsor II (L_2 + excess brine). Addition of cosurfactant decreases the uptake of brine in the microemulsion since an increase in the cosurfactant activity tends to increase the curvature of the interface around the water side. Addition of oil (cyclohexane) decreases the activity of the cosurfactant and increases the uptake of the brine in the microemulsion. Inspired by this titration method we prepared Winsor II systems with small amounts of excess brine by adding small amounts of cosurfactant to homogeneous L_2 phases at the phase boundary L_2/Winsor II.

Analytical procedures. Salt concentrations were measured by potentiometric titration of the chloride ion with a 0.10 M silver nitrate solution. For this purpose we used an automatic titration system manufactured by Mettler, consisting of an electrode potential amplifier DK 10, a rate and end point controller DK 11, and an automatic burette DV 11. The indicator electrode was a small silver electrode. The reference electrode, a calomel electrode in a saturated KCl solution, was connected to the measuring cell with a Vycor tip (EG + G/Parc). No significant leakage of chloride ions through the salt bridge could be detected. The titrations were done in a 3% KNO₃ solution to maintain a constant ionic strength and to maintain a constant diffusion potential at the salt bridge. To avoid traces of SDS in the water phase, a small amount of barium nitrate was added before titration. The measurements were reproducible to within 0.1%.

The amount of water in the oil phase was determined with a gas chromatograph equipped with a thermal conductivity detector. The dispersed volume of water (V_w^M) was obtained by subtraction of the amount of water dissolved in the continuous oil phase. The latter quantity was measured in systems without surfactant (but with cosurfactant).

3. EXPLORING THE EFFECT OF SALT PARTITIONING

The importance of the salt partitioning becomes evident from the following experiment. A series of Winsor II microemulsions that have a volume of excess brine much smaller than the volume of dispersed brine was produced by the method described in the experimental section. The effect of the partitioning of salt can be seen from Table 1, where the salt concentration in the excess brine (c_{el}) is listed for various salt concentrations (c_{el}^i) in the brine before mixing and various brine/surfactant ratios (W_0) in the microemulsion phase. In these experiments the pentanol concentration in the oil is variable, since it has to be adapted to the salt concentration and to W_0 in order to be close to the L_2/Winsor II boundary. Because only a very small amount of brine is separated from the microemulsion phase, the average salt concentration in the microemulsion droplets remains approximately equal to c_{el}^i.

A striking observation from this table is the considerable increase of the salt concentration, which may even be as large as a factor of 3. Because of the sensitivity of these microemulsion systems towards the salt concentration, the effect of the salt partitioning is clearly not negligible and will have large effects on the phase behavior of the system. Furthermore it appears from Table 1 that the concentration of salt measured in the excess brine is always larger than in the initial brine, and that the relative increase is larger for low salt
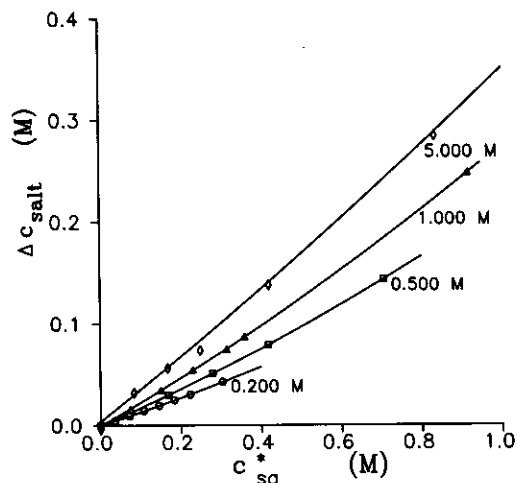
TABLE 1

Initial Salt Concentrations (c_{el}^i) and Salt Concentrations (c_{el}) (Measured and Theoretical) in the Excess Brine of Winsor II Microemulsions Close to the L_2/Winsor II Boundary

		c_{el} (M)	
W_0 (w/w)	c_{el}^i (M)	Experimental	Theoretical
1.74	0.200	0.775	0.559
1.74	0.500	1.047	1.087
3.47	0.0500	0.176	0.133
3.47	0.100	0.232	0.212
3.47	0.200	0.359	0.358
3.47	0.500	0.714	0.756
5.20	0.150	0.239	0.239
5.20	0.200	0.294	0.302
5.20	0.300	0.409	0.424
6.94	0.150	0.216	0.215

FIG. 1. The increase of the salt concentration Δc_{salt} in the excess aqueous phase as a function of the surfactant concentration c_{sa}^*, for systems with pentanol as the cosurfactant (equilibrium concentration in oil 20% (w/w)) at four different initial salt concentrations. Ambient temperature 24.7 $\pm 0.2°C$.

concentrations and small values of W_0. The absolute increase becomes smaller for larger values of W_0.

To obtain a better understanding of these observations we systematically investigated the increase of the salt concentration in the excess brine of Winsor II systems with a large amount of excess brine. In these systems the increase of the salt concentration remains relatively small because the amount of excess brine is now much larger than the amount of brine in the microemulsion phase. Figure 1 shows the increase of the salt concentration in the excess water phase as a function of the surfactant concentration c_{sa}^* and at various initial salt concentrations. The increase of the salt concentration is defined as $\Delta c_{salt} = c_{el} - c_{el}^0$, where c_{el}^0 is the salt concentration in the excess brine for systems without SDS. A precise definition of the surfactant concentration c_{sa}^* will be given later (Eq. [6]), but it is to a very good approximation equal to the amount of surfactant divided by the total volume of brine in the system. To be sure that SDS did not contain interfering amounts of SO_4^{2-}, which would contribute to the measured Δc_{salt} values, we checked for sulfate ions (addition of barium nitrate) in the excess phase of a Winsor II system with large amounts of SDS. We also found no indication that other ions which would precipitate with silver nitrate are present in SDS. From Fig. 1 we observe that the salt concentration increases almost linearly with the surfactant concentration, and the data points are well represented by second order polynomials ($c_{el} = c_{el}^0 + \mathcal{P}_1 c_{sa}^* + \mathcal{P}_2 (c_{sa}^*)^2$). The fitting parameters are listed in Table 2.

We note that c_{el}^0 is not exactly equal to the salt concentration (c_{el}^i) of the brine before mixing. This is due to the dissolution of the alcohol in water and the solubility of molecular water in the oil, which are both dependent on the

TABLE 2

Experimental Values of $\mathcal{P}_1$ and $\mathcal{P}_2$ for the Polynomial $c_{el} = c_{el}^0 + \mathcal{P}_1 c_{sa}^* + \mathcal{P}_2(c_{sa}^*)^2$. Experimental Conditions: 24.7 ± 0.2°C, 0.20 (w/w) Pentanol in the Oil Continuous Phase

c_{el}^i mol/dm³	c_{el}^0 mol/dm³	$\mathcal{P}_1$	$\mathcal{P}_2$ dm³/mol
0.200	0.1989	0.127	0.042
0.500	0.4969	0.170	0.048
1.000	0.9961	0.225	0.051
5.000	5.017	0.31	0.04

salt concentration (salting-out). At low salt concentrations the combined effect leads to a lower value of c_{el}^0 compared to c_{el}^i, whereas at high salt concentrations c_{el}^0 becomes larger than c_{el}^i. The measured differences between c_{el}^0 and c_{el}^i agree within experimental error with calculations based on measurements of the solubility of water in the oil phase (19) and the distribution of pentanol between oil and brine (as obtained from Refs. (20, 21)).

4. THEORY OF SALT PARTITIONING AND COMPARISON WITH EXPERIMENT

Partitioning of salt in Winsor II equilibria. A W/O microemulsion consists of small water pools, hereafter referred to as droplets, that are embedded in a continuous oil phase. These droplets are coated by an adsorption layer of SDS and pentanol. This layer is negatively charged due to the presence of ionic heads of the surfactant. If the surfactant heads are completely ionized, the surface charge density is given by

$$\sigma = -F \cdot \Gamma_{sa}, \qquad [1]$$

where Γ_{sa} is the adsorption density of the surfactant, and F is the Faraday constant. Through interaction with the electric field, a redistribution of the ions in the electrolyte (NaCl) solution inside the microemulsion droplets results in the establishment of an electrical double layer. The co-ions (chloride, and in principle also dodecylsulfate), which undergo negative adsorption, are expelled from the charged surface into the bulk of the droplets and the excess water phase. Since the excess water phase must remain uncharged, this is accompanied by an equivalent expulsion of counterions. As a result we observe an increase of the electrolyte concentration in the excess water phase. Conservation of mass requires

$$(V_w^M + V_w^{ex}) \cdot c_{el} + \Gamma_{co-ion} \cdot A = V_w^i \cdot c_{el}^i, \qquad [2]$$

where V_w^M is the total volume of the water droplets in the microemulsion phase, V_w^{ex} is the volume of the excess water phase, V_w^i represents the volume of the brine before mixing, and Γ_{co-ion} is the interfacial excess (negative) of the co-ions. The total amount of area of the droplet interface A can be

obtained from the amount of surfactant n_{sa} present in the interface and the adsorption density of the surfactant,

$$A = \frac{n_{sa}}{\Gamma_{sa}}. \qquad [3]$$

Substitution of Eq. [3] into [2] and a rearrangement then yield the expression for the electrolyte concentration in the excess water phase,

$$c_{el} = c_{el}^0 - \frac{\Gamma_{co-ion}}{\Gamma_{sa}} \cdot c_{sa}^*, \qquad [4]$$

where c_{el}^0 is the electrolyte concentration in the excess water phase of an equilibrated system in the absence of surfactant,

$$c_{el}^0 = c_{el}^i \cdot \frac{V_w^i}{V_w^M + V_w^{ex}}, \qquad [5]$$

and we define

$$c_{sa}^* \equiv \frac{n_{sa}}{V_w^M + V_w^{ex}}. \qquad [6]$$

V_w^i is not exactly equal to the sum $(V_w^M + V_w^{ex})$, because the solubility of cosurfactant in the water phase increases and the uptake of molecular water in the oil phase decreases the total volume of the water phase. Usually this difference is very small, as can be seen from Table 2. We may therefore introduce the approximations $c_{el}^0 \approx c_{el}^i$ and $c_{sa}^* \approx n_{sa}/V_w^i$.

From Eq. [4] and the relation given in the heading of Table 2 it follows that

$$-\frac{\Gamma_{co-ion}}{\Gamma_{sa}} = \mathcal{P}_1 + \mathcal{P}_2 \cdot c_{sa}^*, \qquad [7]$$

and therefore in the limit of $c_{sa}^* \to 0$, where $c_{el} \to c_{el}^0$, we obtain

$$\mathcal{P}_1 = -\frac{\Gamma_{co-ion}(c_{el}^0)}{\Gamma_{sa}}. \qquad [8]$$

So far the relationships are quite general. At this point we need to relate Γ_{co-ion} to σ and c_{el}. This dependence can be obtained from double-layer theory, adapted to the fact that the water in the microemulsion phase consists of small droplets. The simplest possible model would be that of an assembly of spherical droplets of radius a of the aqueous phase. The radius is then given by

$$a = \frac{3V_w^M}{A} = \frac{3V_w^M \Gamma_{sa}}{n_{sa}} = \frac{3M_{sa}\Gamma_{sa}}{D_w} \cdot W_0. \qquad [9]$$

Here M_{sa} is the molar mass of the surfactant and D_w is the mass density of the aqueous core. A discussion of the influ-

ence of size and shape fluctuations of the droplets is given at the end of this section.

To apply double layer theory to this model the Poisson–Boltzmann equation inside a sphere,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\left(\frac{e\psi}{kT}\right)\right) = \kappa^2\sinh\frac{e\psi}{kT},\qquad [10]$$

has to be solved with given surface charge density σ (see Eq. [1]) as the boundary condition:

$$\sigma = \epsilon_r\epsilon_0\left(\frac{d\psi}{dr}\right)_{interface}.\qquad [11]$$

With ψ known as a function of r, the co-ion adsorption is obtained from

$$\Gamma_{co\text{-}ion} = \frac{c_{el}\int_0^a[\exp(-e|\psi(r)|/kT) - 1]4\pi r^2 dr}{4\pi a^2}.\qquad [12]$$

In these equations e is the charge of a proton, k is the Boltzmann constant, T is the temperature, $\epsilon_r\epsilon_0$ is the dielectric permittivity, and $\psi(r)$ is the potential at distance r from the center of the sphere. For spheres with radius much larger than the Debye screening length κ^{-1}, with κ defined by

$$\kappa = \sqrt{\frac{2F^2c_{el}}{\epsilon_r\epsilon_0 RT}},\qquad [13]$$

and in the limit of high surface potential, Eq. [12] approaches the result (22)

$$\Gamma_{co\text{-}ion} = -2\kappa^{-1}c_{el}^0.\qquad [14]$$

This expression, which is a familiar result for co-ion adsorption in a flat double layer at high surface potential, shows that $\Gamma_{co\text{-}ion}$ is approximately proportional to $\sqrt{c_{el}^0}$.

For a Winsor II microemulsion system with given Γ_{sa}, W_0, c_{sa}^* and c_{el}^0 we first calculate the droplet radius from Eq. [9] and σ using Eq. [1]. Combination of Eqs. [8] and [12] then enables us to calculate $\mathcal{P}_1$. Note that $\Gamma_{co\text{-}ion}$ is dependent on the electrolyte concentration in the excess brine. This concentration is influenced by the amount of salt expelled from the microemulsion phase, which is in turn determined by the co-ion adsorption. Clearly the calculation of the equilibrium salt concentration c_{el} that simultaneously satisfies Eqs. [4] and [12] requires an iterative procedure. For a large increase of the salt concentration this requires a large number of iterations, and in these situations approximate solutions for $\Gamma_{co\text{-}ion}$ are convenient. For this purpose we applied an analytical expression derived by van Aken et al. (22) for the surface excess concentration $\Gamma_{co\text{-}ion}$ for 1:1 electrolytes at bulk

concentration c_{el}, based on the Poisson–Boltzmann equation inside a sphere of radius a. This equation was shown to yield results in excellent agreement ($\pm 2\%$) with numerical analysis, for $\kappa a > 4$ (22).

One may worry about size and shape fluctuations of the droplets. We want to argue that as long as the average size of the water droplets is large compared to the Debye length κ^{-1} (thin double-layers), as is indeed the case here, the effect of size and shape fluctuations on $\Gamma_{co\text{-}ion}$ is small. It can be shown (22) that, for thin double-layers, $\Gamma_{co\text{-}ion}$ consists of a flat double layer term plus a curvature dependent term which to leading order behaves as $1/\kappa a$. Size and shape fluctuations only lead to modifications of the curvature dependent term. Moreover the largest fluctuations are expected for large droplets, where the curvature dependent correction terms are small anyway.

Comparison between theory and experiment. In theoretical calculations of the salt partitioning Γ_{sa} is an important parameter because it is needed to calculate A (Eq. [3]), a (Eq. [9]), and σ (Eq. [1]). Unfortunately this parameter is not accurately known. Values for Γ_{sa} that are reported for the planar oil/water interface show some variation with the salt and pentanol concentrations, and are not completely equal for different authors (17, 20, 21, 23, 24). Γ_{sa} may also depend somewhat on the radius a (25). It was shown by SAXS measurements (20) that at the droplet interface the variation of Γ_{sa} with the pentanol concentration is much less than at the planar interface. Unfortunately the absolute value of Γ_{sa} could not be obtained from these measurements. Therefore, based on the values for the planar interface at pentanol fractions in the oil phase of 0.20 (w/w), $\Gamma_{sa} = 1.76 \times 10^{-6}$ mol/m^2 (at 0.20 M salt) (21), and $\Gamma_{sa} = 1.82 \times 10^{-6}$ mol/m^2 (at 0.30 M salt) (17), we have chosen $\Gamma_{sa} = 1.8 \times 10^{-6}$ mol/m^2 for all salt concentrations and droplet radii.

In Table 3 the experimental values of $\mathcal{P}_1$ are compared with the theoretical values calculated with Eqs. [8] and [12] and numerically calculated co-ion adsorptions. We also performed measurements on systems with heptanol instead of pentanol as the cosurfactant. These results are reported elsewhere (20), and are similar to the results obtained for pentanol. The values for $\mathcal{P}_1$ between brackets in Table 3 are calculated values based on a modified model of the double layer (empty Stern layer) and are discussed at the end of this section. The values for the droplet radii in this table are obtained by linear extrapolation of the water/surfactant ratio measured at finite c_{sa}^*, and the application of Eq. [9].

The last column of Table 3 gives the fraction of salt that is expelled out of the droplet volume. We note that in most cases more than half of the salt is expelled from the droplets. The most extreme case is found for the system with 5 M salt, where the (extremely small) droplets are essentially salt-free.

From Table 3 we see a semiquantitative correspondence between the experimental and theoretical $\mathcal{P}_1$ values. This

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TABLE 3

Experimental and Theoretical Values of $\mathcal{P}_1$ and Droplet Radii at Zero c_{sa}^{*}. Theoretical Values Obtained by Numerical Integration of the Poisson-Boltzman Equation and Assuming $\Gamma_{sa} = 1.8 \cdot 10^{-6}$ mol/m². Values of $\mathcal{P}_1$ in Parenthesis are Corrected for a Stern Layer with Thickness $\delta = 0.2$ nm, See Text for Details. Experimental Conditions: $24.7 \pm 0.2°C$, 0.20 (w/w) Pentanol in the Oil Continuous Phase

c_{in} mol/dm³	c_{el}^0 mol/dm³	Droplet radius nm	κa	Values of $\mathcal{P}_1$		Fraction expelled (%)
				Experimental	Theoretical (Eqs. [8] and [12])	
0.200	0.19891	13.5	20	0.127	0.117 (0.136)	26
0.500	0.49692	3.0	7.0	0.1695	0.145 (0.178)	61
1.000	0.9961	1.6	5.2	0.225	0.173 (0.229)	78
5.000	5.017	0.33	2.4	0.31	0.214 (0.307)	100

agreement between theoretical and experimental values for $\mathcal{P}_1$ shows that the salt partitioning can be attributed to the electrical double layer. However, we also see that the theoretical values are systematically lower than the experimental values, and that this difference becomes larger for higher salt concentrations (smaller droplet radii). This is probably due to inaccuracy of the Poisson–Boltzmann equation, which neglects the finite size of the ions.

We may try to improve the expression for the co-ion adsorption, because for practical applications an accurate expression for the salt concentration in the excess phase is needed. Therefore we follow Biais et al. (10) and introduce a thin salt-free film of thickness δ at the charged droplet interface. This can be regarded as an empirical correction for the finite size of the ions in the diffuse layer and of the hydrated heads of the adsorbed surfactant ion, that was already introduced by Stern (26). This salt-free film increases the negative adsorption of the co-ions, and leads to a higher theoretical $\mathcal{P}_1$ value. Second it is possible that the effective charge density of the surface is decreased by a factor α ($0 < \alpha < 1$), due to partial ionization of the adsorbed surfactant molecules, penetration of counterions between the charged surfactant heads, or specific adsorption of counterions. For the high surface charges and the resulting high surface potentials in this study, Γ_{co-ion} is not very sensitive to variations of α, provided α does not deviate too much from unity. Moreover partial dissociation would lead to a decreased value of $\mathcal{P}_1$ whereas experimentally an increase is found. In our calculations we therefore assume $\alpha = 1$. The theoretical values in parentheses in Table 3 show that the theoretical values for $\mathcal{P}_1$ are in good agreement with the experimental values by choosing $\delta = 0.2$ nm. Apparently only very minor corrections are needed to obtain quantitative agreement with the experiments.

In Table 1 we compare the measured equilibrium salt concentrations to theoretical values, using the empirical correction value $\delta = 0.2$ nm in the expression for the co-ion adsorption. This table clearly shows that the discussed theory

allows us satisfactorily to predict the salt concentration in the excess phase.

5. THE INFLUENCE OF THE DISTRIBUTION OF SALT ON THE PHASE BEHAVIOR OF MICROEMULSION SYSTEMS

Having established that the salt partitioning caused by negative adsorption is a substantial effect, we now illustrate its influence on the phase behavior of microemulsion systems by two examples. From these examples it will be obvious that the phase boundaries of the microemulsion phase under study cannot be interpreted well if one does not take into
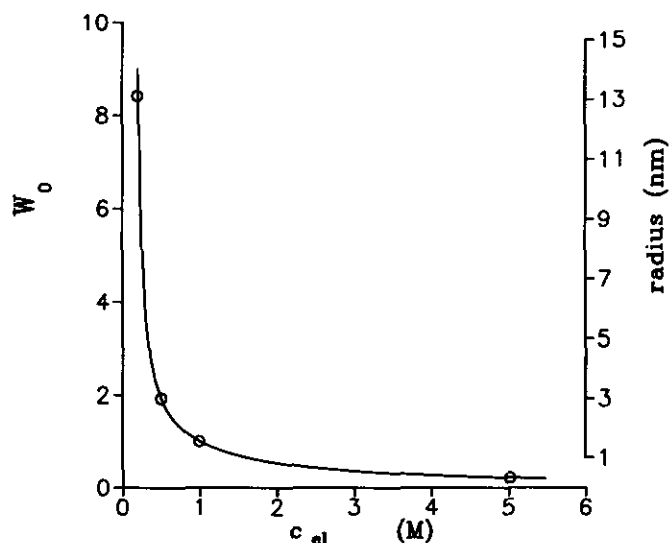

FIG. 2. W_0 and droplet radius of the microemulsion phase of Winsor II systems as a function of the salt concentration in the excess phase. Data points are found by extrapolation to zero surfactant concentration of Winsor II equilibria. The droplet radius is calculated with Eq. [9], setting $\Gamma_{sa} = 1.8 \times 10^{-6}$ mol/m². 0.20 (w/w) pentanol in the oil. Drawn line is meant to guide the eye.

account the increase of the effective salt concentration due to the partitioning of salt.

Example I. A situation in which the salt partitioning is directly reflected in the microemulsion phase behavior is the decrease of the droplet radius in Winsor II systems with increasing surfactant content and at constant initial salt concentration. To appreciate this effect it is important to realize that the value of the equilibrium droplet radius (or equivalently the W_0-value (Eq. [9])) of Winsor II systems strongly decreases with increasing salt concentration. This is demonstrated in Fig. 2, where experimental data for the dependence of W_0 on the salt concentration for a Winsor II microemulsion system at constant pentanol concentration (0.20 (w/w)) in the continuous oil phase are presented. The W_0 values are limiting values, as found by extrapolation to a surfactant content of zero, so that the increase of the salt concentration is absent here.

In Fig. 3 we plotted the measured W_0-value as a function of c_{sa}^* for the series of samples with an initial salt concentration of 0.200 M, for which the c_{el}^0, P_1 and P_2 values were already given in Table 2. W_0 is seen to decrease on increasing the SDS contents, due to the increase of the concentration in the brine resulting from the salt partitioning.

We stress that the variation of W_0 observed in Fig. 3 is not a direct effect of the increase of the volume fraction of microemulsion droplets in the microemulsion phase. Such a volume fraction effect was discussed theoretically (25) and also investigated experimentally (20), and was shown to be of minor importance at the volume fractions in the present
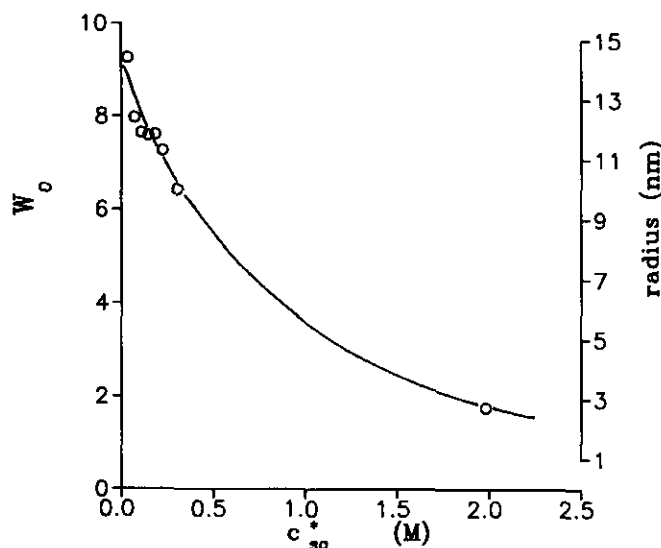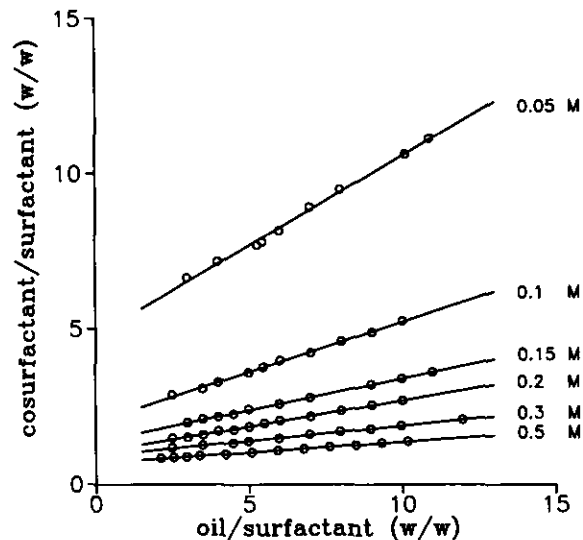

FIG. 4. Experimental dilution lines at the L$_2$/Winsor II phase boundary obtained for $W_0 = 3.47$ (w/w). Dilution lines are marked with their initial salt concentration.

study. Moreover, the effect of an increase of the volume fraction is an increase of the droplet radius rather than a decrease (20, 25).

Example II. In this example we demonstrate that the negative adsorption of salt also influences the behavior of W/O microemulsions in the single phase (L$_2$) region. Here the co-ion adsorption manifests itself by affecting the positions of the phase boundaries, as can be demonstrated experimentally by the establishment of dilution lines.

Single-phase W/O microemulsions with various initial salt concentrations and W_0 values were diluted along the L$_2$/Winsor II phase boundary. Examples of such dilution lines are given in Fig. 4. From the slope of these dilution lines we deduce the composition of the continuous oil phase for microemulsion compositions localized at the L$_2$/Winsor II phase boundary. In Fig. 5 the measured pentanol fractions in the continuous oil phase are plotted as a function of the initial salt concentration in the brine. This is done for four different W_0-values, respectively 1.74, 3.47, 5.20, and 6.94 (w/w). We see that, for constant W_0, the pentanol fraction in the continuous oil phase always decreases on increasing the salt concentration. This is in accordance with the behavior previously described for the Winsor II systems, since both an increase of the salt concentration and an increase of the cosurfactant concentration lead to a decrease of W_0. W_0 can therefore be kept constant by increasing the pentanol concentration and decreasing the salt concentration, and vice versa. However, three of the four curves for different W_0 coincide at a certain point. For salt concentrations lower than this point, W_0 increases on increasing the salt concentration. At first sight this seems to be in contradiction with the influence of the pentanol concentration for the Winsor

FIG. 3. Measured W_0 and estimated droplet radius of the microemulsion phase of Winsor II microemulsion systems as a function of the surfactant concentration. The initial salt concentration was 0.200 M, and the pentanol concentration in the excess oil phase was approximately 0.20 (w/w). The droplet radius is estimated from W_0 with Eq. [9], assuming $\Gamma_{sa} = 1.8 \times 10^{-6}$ mol/m^2. The drawn line is meant to guide the eye.

II equilibria, where we observed the opposite effect. The explanation of this apparent contradiction lies in the distribution of salt. The negative adsorption of co-ions in the electrical double layer at the charged droplet interface leads to an increased salt concentration in the center of the droplets. Although no excess phase is present in the single phase region the effect of the distribution of salt is still present and leads to a considerably higher "effective" salt concentration than in the initial brine.

This effective salt concentration (c_{el}^{eff}) can be obtained by calculating the salt concentration in an infinitesimally small amount of excess brine that is supposed to separate from the microemulsion phase. If we plot the pentanol fractions in the continuous phase of Fig. 5 as a function of the calculated effective salt concentration, the data points move up in such a way that now a regular dependence of W_0 on the pentanol and salt concentration is obtained (Fig. 6). That the calculated quite high values for c_{el}^{eff} are realistic was previously shown in Table 1, where we compared calculated salt concentrations to experimental values for Winsor II systems close to the phase boundary.

Another implication that is obvious from Fig. 6 is the following. It is well established for the system of this study that, at low surfactant concentrations, Winsor II systems cannot be formed at salt concentrations below approximately $0.10 M$ (25, 27). But Fig. 5 evidences the existence of Winsor II systems at initial salt concentration much lower than $0.10 M$. Figure 6, however, shows that the effective salt concentrations for these microemulsion systems were always higher than the lower limit of $0.10 M$.

6. CONCLUSIONS

The concentration of salt in the water droplets of the microemulsion phase of Winsor II microemulsion systems is

FIG. 6. Same as Fig. 5, but now as a function of the calculated effective salt concentration.

significantly lower than in the coexisting excess water phase. We showed that this effect can be attributed to the negative adsorption of salt in the electrical double layer. The experimental values were compared to calculated values based on the Poisson–Boltzmann theory for the electrical double layer. Better agreement between theory and experiments is, however, obtained by the addition of a small empirical Stern correction term that accounts for a thin ion-free water layer around the surfactant heads.

The relative increase of the salt concentration in the excess aqueous phase is at its largest for low electrolyte concentration, and small brine/surfactant ratios of the system. The effect of this salt partitioning on Winsor II systems is that the uptake of brine is reduced at high surfactant content. Although for single phase microemulsion systems co-ion adsorption is not directly measurable in the form of an increase of the salt concentration, the effect on the location of the boundary of the single phase L_2-region is evident.

The obvious consequence of this study is that the brine should not be regarded as a pseudocomponent of microemulsion systems. It is, however, possible to correct the experimental results with relatively simple equations for the partitioning of salt.
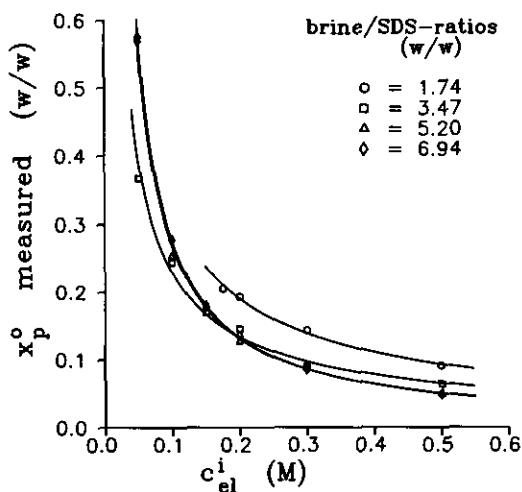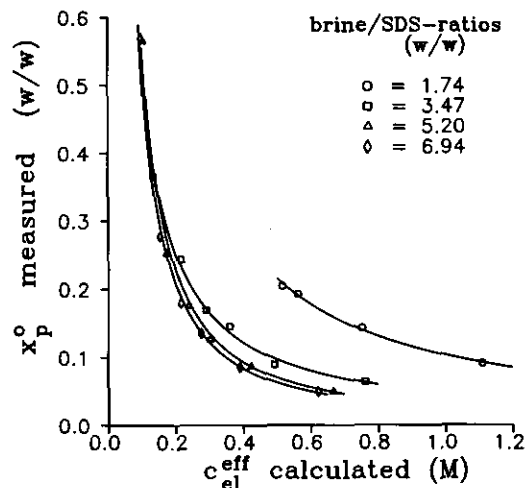
FIG. 5. Pentanol fractions in the continuous oil phase for microemulsions with a maximum water content as a function of the initial salt concentration, at several W_0.

REFERENCES

1. Luisi, P. L., Giomini, M., Pileni, M. P., and Robinson, B. H., *Biochim. Biophys. Acta* **947**, 209 (1988); Luisi, P. L., and Magid, L. J., *Crit. Rev. Biochem.* **20**, 409 (1986).
2. Dekker, M., Hilhorst, R., and Laane, C., *Anal. Biochem.* **178**, 217 (1989).

3. Luisi, P. L., and Laane, C., *Trends Biotech.* **4**, 153 (1986); Luisi, P. L., and Steinman-Hofmann, B., *Methods Enzymol.* **136**, 188 (1987).

4. Hatton, A. T., *in* "Surfactant Science Series, Vol. 33" (J. F. Scamehorn and J. H. Harwell, Eds.), p. 55. Dekker, New York, 1989.

5. Martinek, K., Levashov, A. V., Klyachko, N., Khmelnitski, Y. L., and Berezin, I. V., *Eur. J. Biochem.* **155**, 453 (1986).

6. Verhaert, R. M. D., Hilhorst, R., Vermuë, M., Schaafsma, T. J., and Veeger, C., *Eur. J. Biochem.* **187**, 59 (1990); Verhaert, R. M. D., Tyrakowska, B., Hilhorst, R., Schaafsma, T. J., and Veeger, C., *Eur. J. Biochem.* **187**, 73 (1990); Tyrakowska, B., Verhaert, R. M. D., Hilhorst, R., and Veeger, C., *Eur. J. Biochem.* **187**, 81 (1990).

7. Tosh, W. C., Jones, S. C., and Adamson, A. W., *J. Colloid Interface Sci.* **31**, 297 (1969).

8. van Nieuwkoop, J., and Snoei, G., *J. Colloid Interface Sci.* **103**, 400 (1985).

9. Fletcher, P. D. I., *J. Chem. Soc. Faraday Trans. 1* **82**, 2651 (1986).

10. Biais, J., Barthe, M., Bourrel, M., Clin, B., and Lalanne, P., *J. Colloid Interface Sci.* **109**, 576 (1986).

11. de Bruyn, P. L., Overbeek, J. Th. G., and Verhoeckx, G. J., *J. Colloid Interface Sci.* **127**, 244 (1989).

12. Adamson, A. W., *J. Colloid Interface Sci.* **29**, 261 (1969).

13. Luisi, P. L., Bonner, F. J., Pellegrini, A., Wiget, P., and Wolf, R., *Helv. Chim. Acta* **62**, 740 (1979).

14. Dossena, A., Rizzo, V., Marchelli, R., Casnati, G., and Luisi, P. L., *Biochim. Biophys. Acta* **446**, 493 (1976).

15. Bourrel, M., and Schechter, R. S., *in* "Microemulsions and Related Systems," Surfactant Science Series, Vol. 60, p. 264. Dekker, New York, 1988.

16. A preliminary version of this work was presented in van Aken, G. A., *in* "The Structure, Dynamics and Equilibrium Properties of Colloidal Systems" (D. M. Bloor and E. Wyn-Jones, Eds.), p. 279. Kluwer Academic, Dordrecht 1990.

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

18. Bowcott, J. E., and Schulman, J. H., *Z. Elektrochem.* **59**, 283 (1955).

19. Huyskens, P. L., Haulet-Pirson, M. Cl., Hanssens, I., and Mullens, J., *J. Phys. Chem.* **84**, 28 (1980).

20. van Aken, G. A., "A Study of Winsor II Microemulsion Equilibria," Doctoral Thesis, Utrecht, 1990.

21. Kegel, W., van Aken, G. A., Bouts, M., Lekkerkerker, H. N. W., Overbeek, J. Th. G., and de Bruyn, P. L., *Langmuir* **9**, 252 (1993).

22. van Aken, G. A., Lekkerkerker, H. N. W., Overbeek, J. Th. G., and de Bruyn, P. L., *J. Phys. Chem.* **46**, 6468 (1990).

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

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

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

26. Stern, O., *Z. Elektrochem.* **30**, 508 (1924).

27. Verhoeckx, G. J., "On Understanding Microemulsions," Doctoral Thesis, Utrecht, 1986.