

# Connection of Ion and Water Exchange between an Aqueous and a Microemulsion Phase

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The exchange of ions and water between an aqueous and a micellar Me-AOT phase (AOT = bis(2-ethylhexyl)sulfosuccinate dissolved in isooctane) was measured in a stirred cell for different states of convection. It was proved experimentally that the water as well as the ion fluxes were controlled by an interfacial process, which therefore can be studied by mass transfer kinetics. The limitation of mass transfer by the interfacial process was manifested by always realized regions of convection independent fluxes (plateau mass transfer rates). In this work it was shown that the water concentration in the micellar phase was controlled by the specific pair and phase distribution of the exchanging cations. In this case, if in both phases cations of main group elements ( $\text{Na-AOT}_o/\text{Sr}_{aq}$ ) and cations of the transition elements ( $\text{Zn-AOT}_o/\text{Ni}_{aq}$ ) were present and exchanging with each other, the equilibration took place without change of the concentration of water (equilibrium value); that is, the micellar sizes remained constant. In the case that Na-AOT in isooctane solution was in contact with an aqueous solution of different transition cations, the water concentration exhibited a pronounced minimum in the micellar phase during mass transfer. In contrast the exchange of a micellar transition cation by sodium ions from the aqueous phase was accompanied by a maximum of the micellar water content during the course of equilibration. The differences in behavior of the micellar water content during equilibration can be related to the known characteristic differences in the micellar AOT head group area for main and transition group counterions. In the system with a pair of two main group or two transition cations undergoing ion exchange, the micelles docking at the interface maintain their individuality, due to the same AOT packing at the micellar and at the macroscopic interface (docking mechanism). However, if an AOT gradient existed between the docked micelles and the interface, caused by the combination of main group and transition cations, partial merging of the micelles accompanied by AOT spreading takes place with an increase or a decrease of the micellar sizes depending on the ion pair and the direction of ion exchange (Marangoni mechanism). In this work some characteristic examples of mass transfer behavior were presented. This behavior could be explained by the two different mechanisms of interfacial solubilization.

## Introduction

The investigations of the two past decades reveal that reverse micelles in apolar media are capable of solubilizing hydrophilic molecules such as electrolytes or proteins inside the aqueous core of the micellar aggregates.<sup>1–3</sup> Such microemulsions are of interest for instance as separation media for proteins,<sup>4,5</sup> and they also can be used as microenvironments for enzymatic reactions.<sup>1–3</sup>

The research activities directed to experimental and theoretical studies at the starting point of our investigations were exclusively restricted to equilibrium states.<sup>4,5</sup> Our experience in chemical mass transfer<sup>6</sup> initiated this research in which the kinetics of two phase solubilization was studied. The knowledge of the kinetics is important for the separation technology as well as for the relevant mass transfer mechanism. During the last years we have reported in different publications the rather unexpected result of a slow rate of ion exchange between a micellar phase (reverse sodium AOT micelles in isooctane) and an aqueous solution for different cations.<sup>7–9</sup> Additionally, it was possible to demonstrate that the rate of ion exchange was controlled by an interfacial step, and therefore the “communication” of micelles with the macroscopic liquid/liquid interface became accessible.

Concerning the interfacial mechanism of solubilization in a first approach, we proposed a spontaneous aggregation of

micelles at the macroscopic interface as the site of the solubilization process.<sup>7</sup> Later on it was necessary to reject this explanation because of the observed strong connection of the rate of solubilization with the micellar concentration. Considering this behavior, the so-called bud or docking mechanism was proposed, which implies the influence of micellar collisions with the liquid/liquid interface on the rate of ion exchange.<sup>9,10</sup> The consecutively occurring three steps, sticky collision, ion exchange between the micellar buds and the aqueous bulk, and fusion of the micellar shell, could then plausibly explain the observed influence of the AOT concentration.

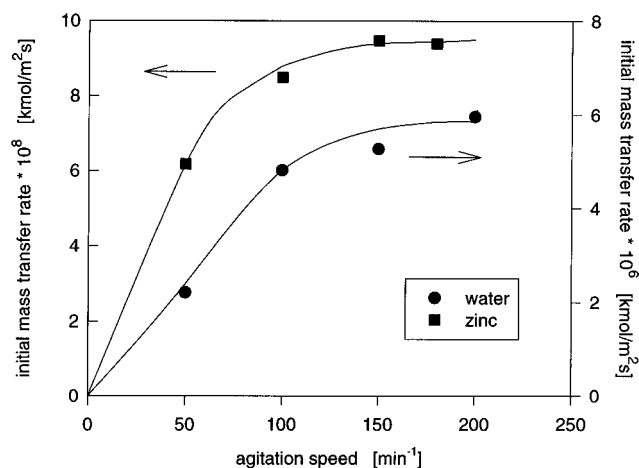
The suggestion in this research program was initiated by the occasionally observed behavior of the water content in the micellar phase, which exhibits a maximum<sup>7</sup> or a minimum<sup>11</sup> value during the ion exchange. These phenomena, being connected with the change of micellar sizes, cannot be interpreted with the proposed docking mechanism. Therefore it was the defined goal of this work to start a systematic series of ion exchange measurements with special attention to the fluxes of water between the phases.

## Experimental Section

The measurements of mass transfer between aqueous and micellar phases were performed in a stirred cell, which is an approved apparatus for the investigation of mass transfer between liquid phases. The important features of this apparatus ( $V = 442 \text{ cm}^3$  for each phase,  $F = 44.2 \text{ cm}^2$ ) are already described elsewhere.<sup>7,12</sup>

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**Figure 1.** Influence of agitation speed on the rate of mass transfer [AOT] = 0.050 kmol/m<sup>3</sup>;  $w_{o,eq}$  = 31.7;  $[Zn^{2+}]_0$  = 0.50 kmol/m<sup>3</sup>.

The mass transfer for different states of convection was measured (concentration measurements in the micellar phase) in order to determine the plateau region, where the rate of mass transfer was limited by an interfacial process. The water content of the micellar phase was expressed in values of  $w_o = ([H_2O]/[AOT])_o$ . Subsequent experiments in related systems were carried out at a sufficiently high state of convection without measuring the convection dependency for every ion concentration.

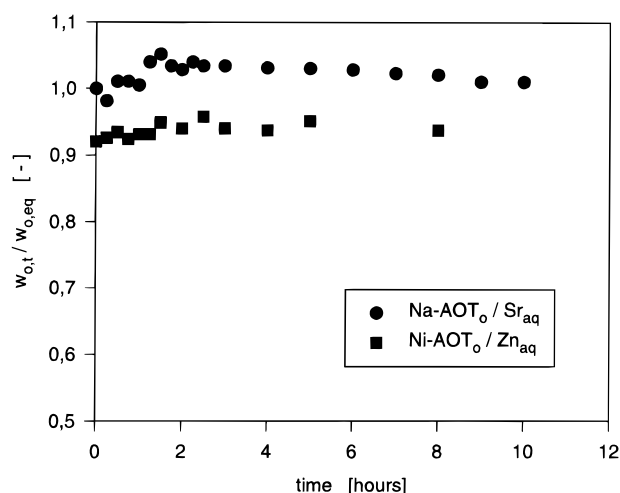
The concentration of metal ions was measured by atomic absorption spectroscopy (SP 9, Pye Unicam) with an accuracy of  $\pm 2\%$ . For the water contents of the micellar phase the Karl Fischer titration (633 Karl-Fischer Automat, Metrohm, Switzerland) was applied (accuracy of  $\pm 3\%$ ). AOT was used as delivered by Fluka without further purification: all other chemicals used were of analytical grade or better. The solvent used for AOT in most cases was isooctane, and in most experiments the selected concentration for AOT was  $5.0 \times 10^{-2}$  kmol/m<sup>3</sup>. The different Me-AOT salts were prepared from Na-AOT by the procedure described by Kitahara et al.<sup>13</sup>

It was of major importance to "presaturate" the micellar phase with pure water before starting the mass transfer experiment. This implies the injection of a calculated amount of water into the AOT solution that corresponds to the predetermined content of micellar water in the equilibrium state for every individual kinetic experiment.

## Results and Discussion

**Rate-Controlling Processes. Ion Exchange.** The results of zinc ion exchange (Figure 1) out of the aqueous phase into the micellar phase (Na-AOT) show that in the convection independent range (plateau region) an interfacial process is rate controlling. This conclusion is justified for our type of stirred cell which was calibrated for various types of kinetic behavior.<sup>6</sup> In the case of a slow transport process a linear increase of the fluxes with the increase of agitation speed  $n_o$  ( $n_{aq}/n_o = \text{const}^{12}$ ) was observed, whereas in processes where the interfacial reaction is the rate-determining step, measured fluxes are independent of the convective flow ("plateau region").<sup>6</sup> Therefore measurements of mass transfer for variable convection in both borderline cases allow distinguishing with high reliability which kind of kinetic behavior takes place.

**Exchange of Water.** In Figure 1 the observed simultaneous fluxes of water out of the micellar phase are also plotted for different states of convection. For the plateau region obtained



**Figure 2.** Constancy of the micellar water concentration in the systems: Na-AOT<sub>0</sub>/Sr<sub>aq</sub> and Ni-AOT<sub>0</sub>/Zn<sub>aq</sub> [AOT] = 0.050 kmol/m<sup>3</sup>;  $[Sr^{2+}]_0$  = 0.50 kmol/m<sup>3</sup>;  $[Zn^{2+}]_0$  = 0.50 kmol/m<sup>3</sup>;  $n_o$  = 150 min<sup>-1</sup>; strontium,  $w_{o,eq}$  = 9.5, zinc,  $w_{o,eq}$  = 31.4.

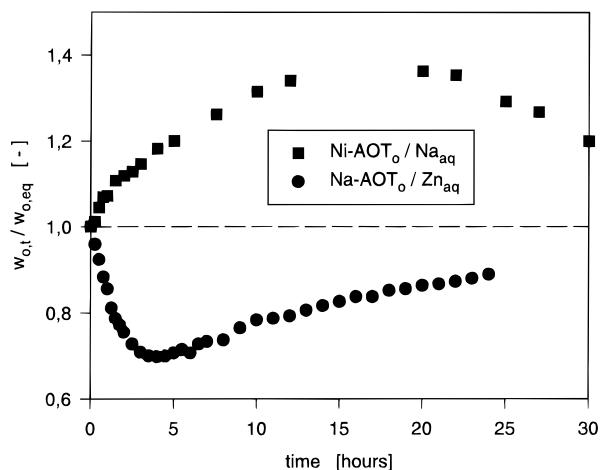
in the range of higher stirring speed it can be concluded that the flux of water is also controlled by an interfacial process. This indicates coupling between the interfacial fluxes of the ions and of water.

Related to both exchange processes (water and ions) for the states of interfacial control (plateau region) a jump of the chemical potential across the interface must exist. This potential difference reflects the nonequilibrium state at the interface. The nonequilibrium state might be caused by the sizes of the micelles, by the composition of the desorbing micelles, or by gradients of interfacial tension. Nevertheless, for the plateau region of fluxes concentration gradients between the bulk phases and the interface can be neglected.

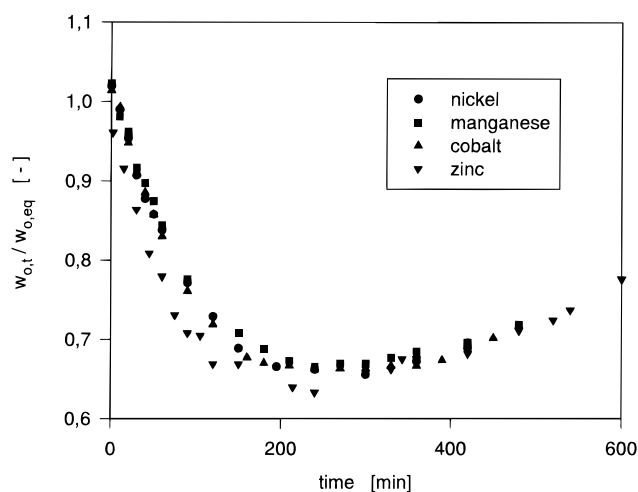
**Fluxes of Water for Different Cation Combinations.** The micellar phase before each experiment was always presaturated with an amount of water adjusted to the equilibrium value  $w_{o,eq}$  for the relevant measurement. This means always defined initial conditions concerning the water content of the micellar phase. In a first approximation for a mechanistic treatment we assumed a correlation of the values of  $w_o$  with the micellar sizes. For comparable  $f_{AOT}$  values with a presaturated micellar phase constancy of the micellar size during ion exchange can be expected.

The above idea was confirmed by measuring exchange behavior of two main group cations (Na-AOT<sub>0</sub>/Sr<sub>aq</sub> or Na-AOT<sub>0</sub>/Cs<sub>aq</sub>) and also for two transition group cations (Zn-AOT<sub>0</sub>/Ni<sub>aq</sub>). As shown in Figure 2, in both cases the water content in the micellar phase remains constant during ion exchange, and this indicates the constancy of the micellar size in spite of ion exchange.

As demonstrated in Figure 3, the constancy of the water content, which was initially adjusted to the equilibrium value  $w_{o,eq}$ , is not always the case: if sodium ions from the micellar phase are replaced by zinc ions from the aqueous bulk phase, the water content shows a distinct minimum, which implies a temporarily reduced size of the micelles. After the steep decrease in the sizes for  $t < t_{min}$  a rather slow increase of the sizes during extraction time  $t > t_{min}$  can be observed until the system equilibrates in the range between 40 and 50 h. The fact that other divalent transition ions such as manganese, nickel, cobalt, and copper show quantitatively the same behavior (Figure 4) suggests that a general property of transition cations replacing the sodium ions from the initial micelles is responsible for the minimum of the water content.



**Figure 3.** Kinetic course of the water concentration in the micellar phase in the systems: Ni-AOT<sub>o</sub>/Na<sub>aq</sub> and Na-AOT<sub>o</sub>/Zn<sub>aq</sub> [AOT<sup>-</sup>] = 0.050 kmol/m<sup>3</sup>; [Na<sup>+</sup>]<sub>0</sub> = 1.00 kmol/m<sup>3</sup>; [Zn<sup>2+</sup>]<sub>0</sub> = 0.50 kmol/m<sup>3</sup>;  $n_o$  = 150 min<sup>-1</sup>; Ni-AOT<sub>o</sub>/Na<sub>aq</sub>,  $w_{0,eq}$  = 17.2; Na-AOT<sub>o</sub>/Zn<sub>aq</sub>,  $w_{0,eq}$  = 31.7.



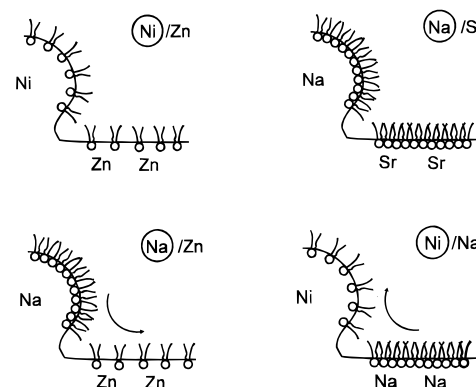
**Figure 4.** Change of water contents in the micellar phase in kinetic experiments for different Na-AOT<sub>o</sub>/Me<sub>aq</sub> systems: Me = Co, Mn, Ni, Zn [AOT] = 0.050 kmol/m<sup>3</sup>; [Me<sup>2+</sup>]<sub>0</sub> = 0.50 kmol/m<sup>3</sup>;  $n_o$  = 150 min<sup>-1</sup>;  $w_{0,eq}$  = 31.7 (Zn); 28.8 (Co); 26.3 (Mn); 30.2 (Ni).

Moreover, the results in Figure 3 demonstrate that for a combination main group/transition group cation the direction of ion fluxes is important too: if nickel ions in the micellar phase are replaced by sodium ions from the aqueous bulk, the water content of the micellar phase passes through a pronounced maximum. This corresponds to a temporary maximum of the micellar sizes during equilibration of the system.

**Exchange Mechanism.** The main question asked was what was the reason for the behavior of the water content of the micellar phase during ion exchange, i.e. constancy, temporary increase or temporary decrease of the micellar sizes.

Changes of micellar sizes caused by the change in the micellar water content can take place only at the macroscopic interface. Thus considerations of a plausible interpretation of the obtained experimental data have to start with the attempt to explain the very different behavior of the ion exchange systems with regard to different interfacial properties of main group and transition group AOT salts.

The sizes of the AOT micelles are accessible for different counterions from PCS,<sup>14</sup> SANS,<sup>15,16</sup> and SAXS<sup>16–18</sup> measurements. It is remarkable that the derived space requirement  $f_{AOT}$  for AOT molecules of the micellar shell was calculated to be  $64 \pm 6 \text{ \AA}^2$  for main group and  $84 \pm 8 \text{ \AA}^2$  for transition cations<sup>15</sup> (SANS). These  $f_{AOT}$  values are related to measurements at a



**Figure 5.** Schematic presentation of the concept "AOT packing gradient".

rather low micellar size ( $w_o = 5$ ), but together with results of former PCS measurements for micellar sizes in the range of  $w_o = 20$ , which gave values of  $48 \text{ \AA}^2$  for main group and  $58 \text{ \AA}^2$  for transition cations,<sup>13</sup> the assumption seems to be justified (for the investigated cations in this work) that main group cations show a more or less similar  $f_{AOT}$  value of the head group area, being lower than the corresponding  $f_{AOT}$  value for the members of the transition cations.

Assuming in a first approximation that the  $f_{AOT}$  values determined for the micellar shells are also representative for the AOT space requirement at the macroscopic interface, an interesting correlation with the observed fluxes of water can be obtained: In the case of the exchange of two main group cations (Na-AOT<sub>o</sub>/Sr<sub>aq</sub>) or two transition cations (Zn-AOT<sub>o</sub>/Ni<sub>aq</sub>) there is no packing gradient between the micellar bud and the macroscopic interface (schema in Figure 5). For such cases constancy of the water content for the micellar phase during equilibration was observed.

For the mass transfer characterized by the exchange of a main group and a transition group cation, however, a packing gradient between the buds and the interface can be expected to be directed from the bud to the interface (Na-AOT<sub>o</sub>/Zn<sub>aq</sub>) or from the interface to the bud (Ni-AOT<sub>o</sub>/Na<sub>aq</sub>) (scheme in Figure 5). In these cases, minimum or maximum values for the micellar water content appear (Figure 3), which can be attributed to the direction of the gradient of AOT packing.

With the convenient assumption for microemulsions that the surfactants (here AOT) are exclusively located at the interfaces (macroscopic or micellar) and a dense packing of AOT molecules at the macroscopic liquid/liquid interface, detailed consistencies are to be expected concerning a lateral movement of AOT molecules (spreading) caused by gradients of the AOT packing at the interface and the buds.

If two main group ions or two transition cations are exchanged between the micellar and the aqueous phase, because of an equal AOT packing at the interface and at the bud, a process of AOT spreading is not to be expected. This agrees with the observed constancy of the water content during ion equilibration, which means constancy of micellar sizes in the organic phase. Therefore the conclusion is justified that for such systems the buds that collided with the interface maintain their individuality during the three-step mechanism: sticky collision, mass transfer, and fusion, as published in former works.<sup>9,10</sup> Related to the conservation of the individual buds, we denote this kind of solubilization as the "docking mechanism".

For such cases, however, where gradients of AOT packing with respect to interfacial pressure (Na-AOT<sub>o</sub>/Zn<sub>aq</sub> and Ni-AOT<sub>o</sub>/Na<sub>aq</sub>) between the buds and the interface do exist, the occurrence of AOT spreading is reasonable to expect. For the

exchange system Na-AOT<sub>o</sub>/Zn<sub>aq</sub> for packing reasons the spreading of AOT from the micellar shell into the macroscopic interface should occur accompanied by a certain merging of the buds. Because of the AOT coverage at the planar interface, the spreading of AOT from a bud into the planar layer means necessarily the formation of secondary buds at the macroscopic interface (Figure 6). If these newly created secondary buds release the interface before the size equilibration at the interface is established, the observed decrease of the water content of the micellar phase is understandable.

In the opposite case, where the AOT packing gradient is directed from the interface toward the buds (Ni-AOT<sub>o</sub>/Na<sub>aq</sub> system), this results in a growing of the buds from the surplus of interfacial AOT, delivered by merging micelles. For this gradient of AOT packing an increase of micellar sizes could be observed, which agrees with the course of water equilibration during ion exchange. The water content of the micellar phase exhibits a maximum value.

Because of the correlation of extreme values for the water content during ion exchange with specific packing gradients, these packing gradients play a key role in the mechanism of mass transfer. An interfacial pressure difference between the micelles and the macroscopic interface should be the driving force for a lateral spreading of AOT molecules, corresponding to a microscopic Marangoni effect. For the conversion from packing gradient to surface pressure difference only a small amount of ion exchange at the neck position of the buds should be enough. As opposed to the "docking mechanism", where the water content of the micellar phase remains constant during kinetic experiments, a "Marangoni mechanism" controls the mass transfer in the case of a pressure gradient between the buds and the interface (water minima or maxima).

**Coupling of the Ion Exchange and the Flux of Water.** Considering the Marangoni mechanism for the exchange system Na-AOT<sub>o</sub>/Zn<sub>aq</sub> as the representative example, a coupling should exist between the flux of zinc ions toward and the flux of water out of the micellar phase, corresponding to the scheme in Figure 6.

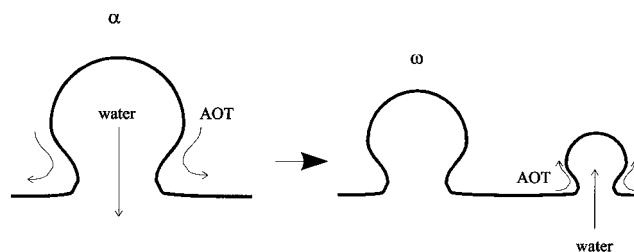
For initial conditions the Na-AOT micellar size is known and is expressed by the adjusted  $w_o$  value. Therefore with a mass balance concerning one primary bud the relation  $\Delta N_w / \Delta N_{Zn}$  can be calculated and compared with the measured flux ratio  $\dot{N}_w / \dot{N}_{Zn}$  for initial conditions.

The assumptions about the change of the  $w_o$  for primary micelles  $\Delta w_{o,p} = (w_{o,p}^\alpha - w_{o,p}^\omega)$  are necessary for the calculation of  $N_w^\dagger$  after sticky collision with the interface. This value was varied in the calculations between  $\Delta w_{o,p} = 30$  (complete merging) and  $\Delta w_{o,p} = 1$ .

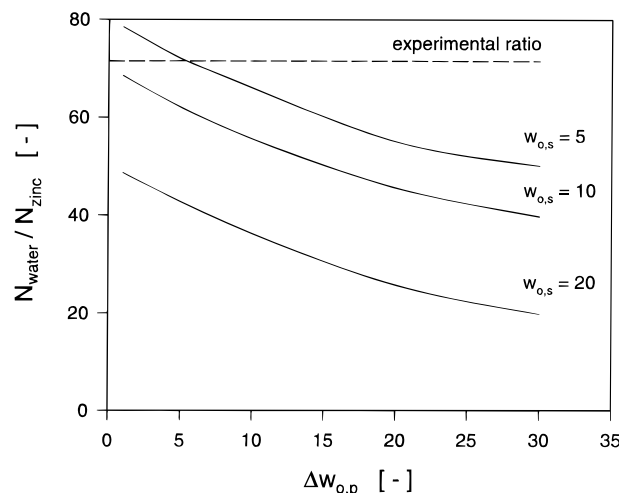
With the known equation<sup>14</sup> for the number of AOT molecules in the micellar shell,

$$N_{AOT} = \frac{36\pi v_w^2}{f_{AOT}} w_o^2 \quad (1)$$

and with reasonable values for the AOT head group area  $f_{AOT}$  ( $f_{AOT} = 48 \text{ \AA}^2$  for Na<sup>+</sup> counterion) the number of spreading AOT molecules  $\Delta N_{AOT}$  corresponding to the assumed  $\Delta w_{o,p}$  is accessible as well as the number of water molecules delivered from a micelle  $N_w^\dagger$  corresponding to  $\Delta w_{o,p}$ . Taking into account that the delivered  $\Delta N_{AOT}$  acts as the source of the secondary micelles, growing at the zinc-loaded macroscopic interface, the solubilization of zinc is determined from electrostatic reasons as  $\Delta N_{Zn} = (1/2)\Delta N_{AOT}$ .



**Figure 6.** Marangoni mechanism of the interactions between micelles and the macroscopic liquid/liquid interface with the formation of secondary micelles.



**Figure 7.** Comparison of calculated and measured ratios of water and zinc transfer (see details in the text).

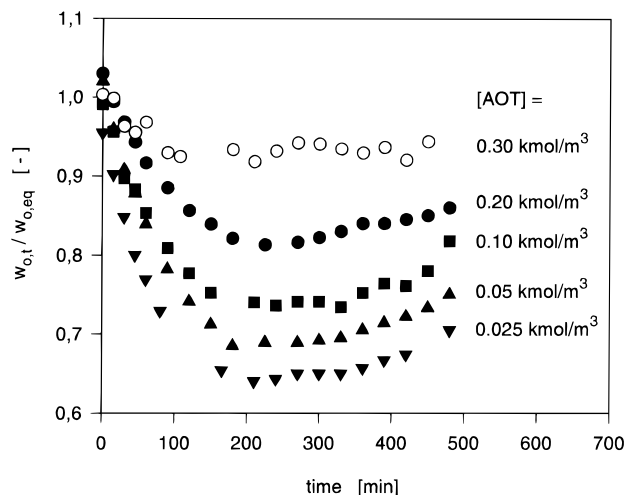
For the calculation of the net number of molecules of water assumptions about the water content of the Zn-AOT secondary micelles  $w_{o,s}$  varying between  $w_{o,s} = 5$  and  $w_{o,s} = 20$  are necessary.

Applying again eq 1 with the head group area  $f_{AOT}$  corresponding to the zinc counterions<sup>15</sup> ( $f_{AOT} = 58 \text{ \AA}^2$ ), with assumed sizes  $w_{o,s}$  and the value of  $\Delta N_{AOT}$ , the corresponding number of created secondary micelles  $N_s$  can be calculated. With the number and the size of the secondary micelles an amount of water  $N_w^\dagger$  is accessible, being combined with formation of the secondary micelles. The net amount of water molecules transferred during the change of one primary micelle to the corresponding secondary micelle is given as  $\Delta N_w = N_w^\dagger - N_w^\alpha$ .

In Figure 7 the calculated ratios  $\Delta N_w / \Delta N_{Zn}$  are plotted against the varied values of  $\Delta w_{o,p}$  with the assumed sizes  $w_{o,s}$  as the parameter and compared together with the measured flux ratio for initial conditions ( $\dot{N}_w / \dot{N}_{Zn}$ ). The ratio of the number of molecules of zinc and water exchanging during the singular act of merging of primary and formation of secondary micelles can be compared with the ratio of fluxes which are integrated values for the total area of mass transfer.

From this comparison a reasonable conclusion can be that, during the unknown residence time of a micellar bud at the interface, the primary micelles ( $w_o = 30$ ) change their sizes in the narrow range ca.  $1 \leq \Delta w_{o,p} \leq 5$ . This result supports the assumption of a very short penetration of zinc ions into the primary micelles with a corresponding low fraction of AOT being spread into the interface. Furthermore, the sizes of the induced secondary micelles can be expected in the range  $5 \leq w_{o,s} \leq 10$ .

**Special Cases of Exchange Kinetics.** Both mechanisms of interaction of micelles with the macroscopic interface allow



**Figure 8.** Influence of the AOT concentration on the minimum of water content of the micellar phase  $[\text{Zn}^{2+}]_0 = 0.50 \text{ kmol/m}^3$ ;  $n_o = 150 \text{ min}^{-1}$ ;  $w_{o,eq} = 23.0$  (0.30); 29.5 (0.20); 31.0 (0.10); 31.7 (0.05); 32.3 (0.025), in parentheses the values of AOT concentration in  $\text{kmol/m}^3$ .

interpretations of further experimental facts, which support retroactively the proposed mechanistic concept.

**Rates of Ion Exchange.** Before this research work the great difference between mass transfer rates of transition (10 times faster) and main group elements for comparable conditions (see Figure 5 in Plucinski and Nitsch<sup>8</sup>) was not understood. However in the system  $\text{Na-AOT}_o/\text{Zn}_{aq}$ , where the enforced secondary micelles are formed from the  $\text{Zn-AOT}$  layer of the interface (Marangoni mechanism), rather high exchange rates of zinc ions can be predicted, compared to the docking mechanism for the system  $\text{Na-AOT}_o/\text{Sr}_{aq}$ , where the ion exchange through the channel of the buds does not reach the equilibrium composition. From the characteristic features of both mechanisms it can be expected that the AOT shell of the desorbed secondary micelles is completely covered with zinc ions, while for the uptake of strontium, primary micelles with a mixed composition of sodium and strontium leave the interface.

**Water Minimum for Different AOT Concentrations.** The water concentration during ion exchange ( $\text{Na-AOT}_o/\text{Zn}_{aq}$ ) shows (Figure 8) that the minimum of the water content becomes less pronounced with the increase of AOT concentration in isooctane. The relevant Marangoni mechanism allows an explanation as follows: with the increase of the micellar concentration the mean distance between primary buds at the interface decreases and causes an increase of lateral AOT flux at the interface, which

finally leads to enlarged secondary micelles. The extreme situation in Figure 8 demonstrates that for  $\text{AOT} = 0.30 \text{ kmol/m}^3$  the secondary micelles grow nearly to the equilibrium size.

**Water Minimum for Different Solvents.** The plots in Figure 9 show that the ion exchange of main group cations ( $\text{Na-AOT}_o/\text{Sr}_{aq}$ ) not only for isooctane but also for *n*-hexane and *n*-decane as the solvent phase for AOT is characterized by a constant concentration of water in the micellar phase during the ion exchange. These results correspond to and support the docking mechanism. However, if sodium from reverse micelles is replaced by zinc ions, for hexane, octane, and decane a minimum value for the water content appears. The water minimum in the case of hexane is much more pronounced than for octane or decane as a solvent. We suppose that, for hexane similarly to the known solvent effect on exchange between micelles in the bulk phase, the solvent changes the rigidity of the AOT layer because penetration into the AOT layer takes place.<sup>19</sup> The increased rigidity might retard the AOT spreading and therefore promotes the formation of small secondary micelles. Decane, because of the larger size of the molecule, cannot penetrate into the AOT palisade layer, and therefore the low rigidity means appropriate spreading and therefore the grow of rather large secondary micelles.

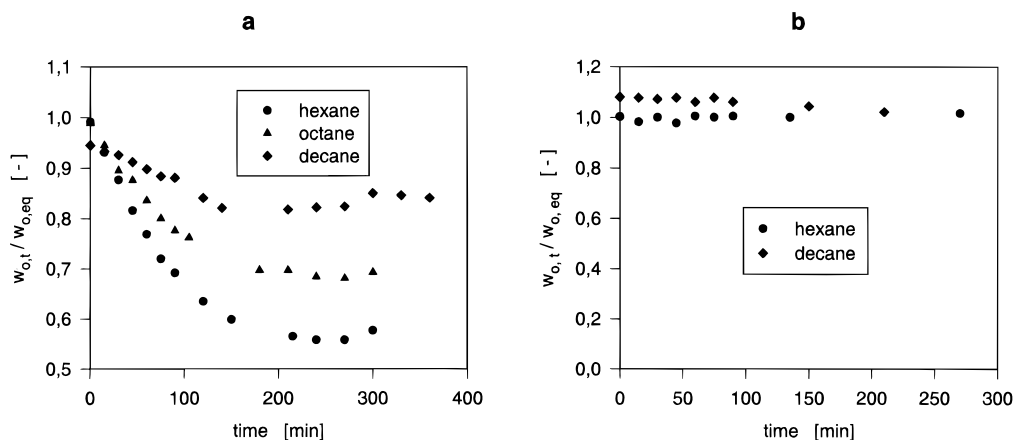
## Conclusions

The important result of this work concerns fluxes of water between an aqueous and a micellar phase caused and directed by the specific ion exchange situation. Because of the proved interfacial limitation of the exchange processes, it was possible to attribute the different experimental results to known interfacial properties of the AOT packing as the guide to the proposed two different mechanisms of solubilization, being directed by the mass transfer between reverse micelles and liquid/liquid interfaces.

It is worth noting, that the collision theory, applied to the interaction of micelles with fluid interfaces with the hypothesis of micellar buds, allows the plausible and experimentally consistent interpretation of mass transfer between the micellar aqueous cores and the aqueous phase being in contact.

Concerning the details, in the context of the proposed bud mechanism the step of shell fusion remains inaccessible, until now. This step determines the residence time of a bud and would be the key for a further quantitative treatment of the single steps of the mechanism, perhaps also for the stated lateral fluxes of AOT (Marangoni mechanism).

Another aspect, in development in our laboratory, concerns the kinetic treatment of the total course of exchange until



**Figure 9.** Role of the solvent on the behavior of water in the micellar phase. (a)  $\text{Na-AOT}_o/\text{Zn}_{aq}$  system  $w_{o,eq} = 29.1$  (*n*-hexane); 31.1 (*n*-octane); 35.0 (*n*-decane). (b)  $\text{Na-AOT}_o/\text{Sr}_{aq}$  system  $w_{o,eq} = 8.5$  (*n*-hexane); 9.8 (*n*-decane)  $[\text{AOT}] = 0.050 \text{ kmol/m}^3$ ;  $[\text{Zn}^{2+}]_0 = [\text{Sr}^{2+}]_0 = 0.50 \text{ kmol/m}^3$ ;  $n_o = 150 \text{ min}^{-1}$ .

equilibration. Special difficulties arise in cases, characterized by extreme values for the water content of the micellar phase. The kinetic treatments demand assumptions about the mass transfer between the micelles during equilibration in the micellar bulk phase.

Finally, it should be emphasized that even for complicated systems kinetics promise to be a very powerful method for exploration, especially if one studies a broad variety of different systems.

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### Symbols

$f_{\text{AOT}}$	area occupied by AOT molecule at the micellar interface
$F$	mass transfer area
Me	metal ions
$n$	agitation speed
$N$	number of molecules
$\dot{N}$	mass transfer rate
$t$	time
$v$	molar volume
$V$	half volume of stirred cell
$w_o$	water ratio $w_o = ([\text{H}_2\text{O}]/[\text{AOT}])_o$

### Subscripts

aq	aqueous
eq	equilibrium
min	minimum
o	organic
p	primary
s	secondary
t	time
w	water
0	initial

### Superscripts

$\alpha$	primary bud after sticky collision
$\omega$	primary bud after merging
$\uparrow$	direction of mass transfer from aqueous to micellar phase
$\downarrow$	direction of mass transfer from micellar to aqueous phase

### References and Notes

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