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# Aqueous micellar and non-micellar effects during the asymmetric hydrogenation of dehydroamino acid derivatives: influence of amphiphiles on enantioselectivity and α-CH/CD exchange

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Dedicated to Professor Dr H. Brunner on the occasion of his 65th birthday

**Abstract**

The effect of different amphiphiles on the CH/CD exchange in the homogeneously catalysed asymmetric hydrogenation/deuteration of methyl (*Z*)-α-acetamidocinnamate or methyl α-acetamidoacrylate in an aqueous micellar medium has been investigated in connection with the effect of amphiphiles on the enhancement of enantioselectivity. In comparison with the exchange of α-CH/CD in water, the amphiphiles inhibit the reaction in the order: cationic < zwitterionic ≪ anionic. In mixtures of cationic (cetyltrimethylammonium hydrogen sulfate, $C_{16}H_{33}N(CH_3)_3^+HSO_4^-$) and anionic amphiphiles (sodium dodecyl sulfate, SDS) the H/D-exchange amount is low in the presence of an excess of SDS, but it increases rapidly near a $CTA^+HSO_4^-$ mole fraction of 0.5 to give a high level of exchange. The enantioselectivity drops to a minimum in the 1:1 mixture because of the low solubility of the cationic–anionic aggregates and the absence of micelles. The results obtained with mixed micelles of Brij 35 (polyethyleneoxide(23) monododecylether, $C_{12}E_{23}$) and SDS are quite different. This mixture is dispersible and able to form micelles over the entire range of mole fractions (0 to 1). As a consequence, the isotope exchange is almost constant from a mole fraction of 0.3–0.9 of SDS. The enantioselectivity is nearly constant over the whole range. The inhibition of H/D exchange in the presence of long-chain alkyl sulfates seems to be caused by a specific interaction with the catalytic rhodium complex. 

*Keywords:* Amphiphiles; Asymmetric hydrogenation; Deuteration; Hydrogen–deuterium exchange; Mechanistic investigations; Micelles

## 1. Introduction

The homogeneously catalysed asymmetric hydrogenation of α-amino acid precursors is one of the best established enantioselective reactions [1]. In particular, the mechanism of the rhodium(I)-complex-catalysed hydrogenation has been investigated by several groups, but was ultimately defined by Halpern [2]. The first results about the stereochemistry of C–H bond formation during the asymmetric reaction were reported independently by Kagan and co-workers [3] and Koenig and Knowles [4] in 1978 by means of deuterium addition. The question of whether an *E*–*Z* isomerization takes place during the reduction of α-acyl amino cinnamic acid derivatives was answered by this method. Ojima et al. [5] used this deuteration method to gain mechanistic insight into the very effective asymmetric induction when chiral phosphino-pyrrolidines were employed as ligands. A relationship between variations in the structure of the substrate and the effect of deuteration was published by Brown and Parker [6]. They used hydrogen deuteride (HD) to determine the isotope effect of the reaction. Later, this method of deuterium labelling was used to compare the mechanisms of hydrogenation and transfer hydrogenation of α,β-unsaturated carboxylic acids [7], where the favoured substrate was itaconic acid. A new phase of development in asymmetric hydrogenation began with the synthesis of

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water-soluble phosphines and the successful application of aqueous two-phase systems [8]. Substitution of $H_2O$ by $D_2O$ resulted in a partial exchange of CH for CD, indicating that water participates as a reactant in asymmetric hydrogenation [9,10]. The extent of deuterium incorporation depends on the nature of the phosphine, the organic solvent and the amount of water present [11]. Scrambling of D or H during the hydrogenation of unsaturated acids or their methyl esters in the presence of $D_2O$, or alternatively in the presence of $H_2O$ for deuteration, implied that rapid β-elimination competes with a slower reductive elimination process. The idea of using this method of deuteration for the synthesis of labelled compounds was developed by Hardick et al. [12].

Changing from a liquid–liquid two-phase system to a micro-heterogeneous micellar system yielded improvements with respect to activity and enantioselectivity in the asymmetric hydrogenation of α-amino acid precursors [13]. Usually, no water-soluble catalytic system is necessary for the solubilization in micelles, but Joo et al. [14] were able to show that micelles can be effective for water-soluble Ru and Rh systems with monosulfonated triphenylphosphine (TPPMS) ligands. Incorporation of D on the basis of $D_2/H_2O$ or $H_2/D_2O$ was clearly retarded in the presence of sodium dodecyl sulfate (SDS) as the micelle-forming amphiphile.

We began to investigate the effect of different amphiphiles on the CH/CD exchange during the asymmetric hydrogenation of α-acetamidoacrylic acid methyl ester and (*Z*)-α-acetamidocinnamic acid methyl ester in aqueous media. In addition to exploring the influence of the micelle formation on activity and enantioselectivity, we wanted to elucidate the mechanism of amphiphile–reactant interactions by means of isotope labelling.

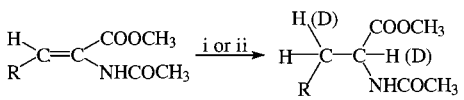
## 2. Results and discussion

Two systems were investigated, the hydrogenation in the presence of $D_2O$, leading to a CH/CD exchange in the α-position, and the deuteration in $H_2O$ as the medium, leading to a preferential CD/CH exchange in the α-position (Scheme 1).

All experiments were carried out using the *N-tert*-butoxycarbonyl-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine (BPPM ) ligand [15] together with a cationic rhodium–(cod)- complex. Two substrates were used: methyl (*Z*)-α-acetamidocinnamate (Table 1) and methyl α-acetamidoacrylate (Table 2). The extent of CH/CD exchange was measured by $^1$H-NMR in the regions between 4.82–4.92 ppm (α-position) and 3.01–3.20 ppm (β-position) and by MS (chemical impact; CI) in the molecular ion region. All experimental data were consistent. All tables contain data for the rate of hydrogenation, the enantioselectivity and for CD (or alternatively CH) exchange in the α-position, with respect to different solvent systems and different surfactants in aqueous media.

The concentration of surfactants was above the critical micelle concentration (CMC) in all examples, except for the non-micellar sodium hexyl sulfate (SHS) and the sodium decyl sulfate (SDeS), which has a relatively high CMC. Whereas SHS gave no useful CH/CD exchange data due to rhodium precipitation, the effect of SDeS was poor for both the activity and enantioselectivity but high for the inhibition of CH/CD exchange (Table 1). This seems to be important to get an idea from the influence of the micelle formation.

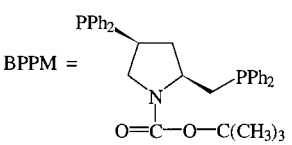
Table 2 contains selected results of CH and CD exchange experiments with the water-soluble substrate methyl α-acetamidoacrylate. It is obvious that the activity in water or $D_2O$ is relatively high (because of the solubility), but the enantioselectivity is very low, and with the (*S*)-configuration and the CH/CD exchange is




R = H (ae), Ph (AE) (0.5 mmol)

i = 0.1 MPa $H_2$, 0.005 mmol $[Rh(cod)_2]BF_4$ + 0.005 mmol BPPM, 0.1 mmol surfactant
7.5 ml $D_2O$, 25° C

ii = 0.1 MPa $D_2$, 0.005 mmol $[Rh(cod)_2]BF_4$ + 0.005 mmol BPPM, 0.1 mmol surfactant,
7.5 ml $H_2O$, 25° C




Scheme 1. Asymmetric hydrogenation of unsaturated amino acid derivatives in water.

Table 1
Deuteration (hydrogenation) of methyl (*Z*)-α-acetamidocinnamate in $H_2O$ ($D_2O$) using $[Rh(cod)_2]BF_4$ and BPPM. Effect of different surfactants on the H/D exchange. Reaction conditions: 25°C; 0.1 MPa $D_2$ or $H_2$; 7.5 ml $H_2O$ or $D_2O$; 0.5 mmol methyl (*Z*)-α-acetamidocinnamate; 0.005 mmol $[Rh(cod)_2]BF_4$; 0.005 mmol BPPM; in situ preparation of catalyst; 0.1 mmol surfactant

| System | Amphiphile[a] | *t*/2 (min) | e.e. *R* (%) | Exchange | |
|---|---|---|---|---|---|
| | | | | %CH $D_2/H_2O$ | %CD $H_2/D_2O$ |
| $D_2/H_2O$ | Without in $H_2O$ | 180 Rh↓ | 83 | 41 | |
| $H_2/D_2O$ | Without in $D_2O$ | 8 h Rh↓ | 78 | | 30 |
| $D_2/CH_3OH$ | Without in $CH_3OH$ | 2 | 92 | 2 | |
| $H_2/CH_3OD$ | Without in $CH_3OD$ | 3 | 93 | | 2 |
| $D_2/H_2O$ | $R_4N^+HSO_4^-$ | 4 | 97 | 40 | |
| $H_2/D_2O$ | $R_4N^+HSO_4^-$ | 6 | 94 | | 27 |
| $D_2/H_2O$ | $R_4N^+CF_3SO_3^-$ | 130 | 80 | 43 | |
| $H_2/D_2O$ | $R_4N^+CF_3SO_3^-$ | 265 | 77 | | 29 |
| $D_2/H_2O$ | $R_4N^+BF_4^-$ | 110 | 81 | 43 | |
| $H_2/D_2O$ | $R_4N^+BF_4^-$ | 140 | 78 | | 31 |
| $D_2/H_2O$ | Brij 35 | 4 | 95 | 44 | |
| $H_2/D_2O$ | Brij 35 | 3 | 94 | | 23 |
| $D_2/H_2O$ | $R_4N^+[CH_3OSO_3]^-$ | 3 | 94 | 33 | |
| $H_2/D_2O$ | $R_4N^+[CH_3OSO_3]^-$ | 5 | 91 | | 22 |
| $D_2/H_2O$ | HDAPS | 3 | 95 | 29 | |
| $H_2/D_2O$ | HDAPS | 12 | 94 | | 23 |
| $D_2/H_2O$ | SHS | 88 Rh↓ | 82 | 25 | |
| $H_2/D_2O$ | SHS | 100 Rh↓ | 80 | | –[b] |
| $D_2/H_2O$ | SDeS | 25 | 73 | 16 | |
| $H_2/D_2O$ | SDeS | 24 | 78 | | 11 |
| $D_2/H_2O$ | SDS | 2 | 95 | 15 | |
| $H_2/D_2O$ | SDS | 5 | 90 | | 9 |
| $D_2/H_2O$ | SHDS | 5 | 93 | 16 | |
| $H_2/D_2O$ | SHDS | 8 | 89 | | 9 |
| $H_2/D_2O$ | Na-dodecylsulfonate | 6 | 97 | 19 | |
| $H_2/D_2O$ | Na-dodecylsulfonate | 7 | 96 | | 10 |
| $D_2/H_2O$ | Na-palmitoylprolinate | 4 | 94 | 34 | |
| $H_2/D_2O$ | Na-palmitoylprolinate | 15 | 92 | | 17 |

[a] HDAPS: hexadecyldimethylammoniumpropanesulfonate; SHDS: sodium hexadecylsulfate; $R_4N^+$: (hexadecyltrimethylammonium)$^+$.
[b] Not possible to analyse.

Table 2
Deuteration (hydrogenation) of methyl α-acetamidoacrylate in $H_2O$ ($D_2O$) using $[Rh(cod)_2]BF_4$ and BPPM. Effect of different surfactants on the H/D exchange. Reaction conditions: 25°C; 0.1 MPa $D_2$ or $H_2$; 7.5 ml $H_2O$ or $D_2O$; 0.5 mmol methyl α-acetamidoacrylate; 0.005 mmol $[Rh(cod)_2]BF_4$; 0.005 mmol BPPM, in situ preparation of catalyst, 0.1 mmol surfactant

| System | Amphiphile[a] | *t*/2 (min) | e.e. *R* (%) | Exchange | |
|---|---|---|---|---|---|
| | | | | %CH $D_2/H_2O$ | %CD $H_2/D_2O$ |
| $D_2/H_2O$ | Without in $H_2O$ | 18 Rh↓ | 6 (*S*) | – | |
| $H_2/D_2O$ | Without in $D_2O$ | 17 Rh↓ | 6 (*S*) | | – |
| $D_2/H_2O$ | $R_4N^+HSO_4^-$ | 3 | 74 | 54 | |
| $H_2/D_2O$ | $R_4N^+HSO_4^-$ | 3 | 64 | | 35 |
| $D_2/H_2O$ | SDS | 3 | 79 | 9 | |
| $H_2/D_2O$ | SDS | 3 | 68 | | 5 |
| $D_2/H_2O$ | Na-dodecylsulfonate | 3 | 83 | 17 | |
| $H_2/D_2O$ | Na-dodecylsulfonate | 3 | 63 | | 10 |

[a] $R_4N^+$: (hexadecyltrimethylammonium)$^+$.

not reliable because of the precipitation of rhodium during the reaction. Addition of 20 mol% of cetyltrimethylammonium hydrogen sulfate increased the enantiomeric excess (e.e.) value to 80% e.e. (system $D_2/H_2O$) directed to the (*R*)-configuration. CD or CH exchange was more significant than without the am-

phiphile, and we propose a reaction with water or $D_2O$ being activated on the surface of the micelle. The influence of SDS on activity and enantioselectivity is quite similar, but the CH and CD exchange is much lower (9% CH and 5% CD), showing a specific effect of sulfate as an anionic amphiphile. Sodium dodecanesulfonate, in comparison, gave a large increase in enantioselectivity, as well as a slightly higher exchange of CH or CD during the hydrogenation. The exceptional position of SDS as an isotope-exchange-inhibiting amphiphile is more evident with methyl α-acetamido-acrylate as the substrate than with methyl (*Z*)-α-acetamidocinnamate (see Tables 1 and 2).

Comparing CD and CH exchange, we observed an isotopic effect [16], meaning that the incorporation of H is faster than the incorporation of D. A graphical presentation of this effect is given in Fig. 1.

The CH or CD exchange in the catalysed hydrogenation is coupled with the hydrogenation process and not observable when the educts are substituted by the products (methyl α-acetamidophenylalaninate or methyl α-acetamidoalaninate) under the reaction conditions.

The ratio of incorporation is noted for each system in parentheses and was found to be between 1.3 and 1.7. This is comparable to the isotope effect of 1.22 reported by Brown and Parker [6] as the ratio of hydrogenation to deuteration for the reaction of (*Z*)-α-acetamidocinnamic acid with HD in methanol using the precatalyst (1.2-bicyclo[2.2.1]heptadiene)(1.2-bis(diphenylphosphino)ethane)rhodium(I) tetrafluoroborate.

Both Table 1 and Fig. 1 show a dependence of the CH/CD exchange on the type of the amphiphile, with a decrease of incorporation in the order cationic, nonionic, zwitterionic and anionic. Low rates of exchange occur especially with SDS. In comparison with the control value in water, the addition of surfactants led to an enhancement of the enantioselectivity. Comparison of the isotope exchange in water and methanol shows that there is an extreme solvent effect, which has been discussed by Sinou and co-workers for 1:1 mixtures of water and different organic solvents [10]. We were interested in the investigation of the CH/CD exchange within a systematically varied mixture of $CH_3OD$–$D_2O$, the results of which are given in Fig. 2.

The graphical presentation shows a non-linearity between isotope incorporation and the mole fraction of $D_2O$ in O-deuterated methanol. In the region with a low $CH_3OD$ or $D_2O$ content the D incorporation is significant, and in the large region between 30 and 80 mol% of $D_2O$ the exchange is almost constant. We conclude that the change of the hydrogen bonding structure in water is extreme, with either a low content of methanol and, vice versa, in methanol with a low content of water. This should influence the activity and reactivity of water in isotope-exchange experiments. Additionally, the curve of enantioselectivities is approximately constant within the mixtures and drops dramatically only from 10 mol% of methanol to pure $D_2O$, most probably due to the low solubility of the reactants in water.

Fig. 3 displays the results of D-labelling experiments in mixed micelles with different ratios of SDS and $CTA^+HSO_4^-$. The isotopic exchange is almost constant with an excess of SDS and rapidly increases at a 1:1 mixture to give a high-level exchange, which is characteristic for $CTA^+HSO_4^-$. The enantioselectivity observed has a minimum at the 1:1 mixture. It is well known that mixtures of anionic and cationic surfactants give a precipitation of ion pairs [17]. The concentration of micelle-forming surfactants should be extremely low in 1:1 mixtures, with an obvious effect on the enantioselectivity and a less clear effect on the CH/CD exchange.

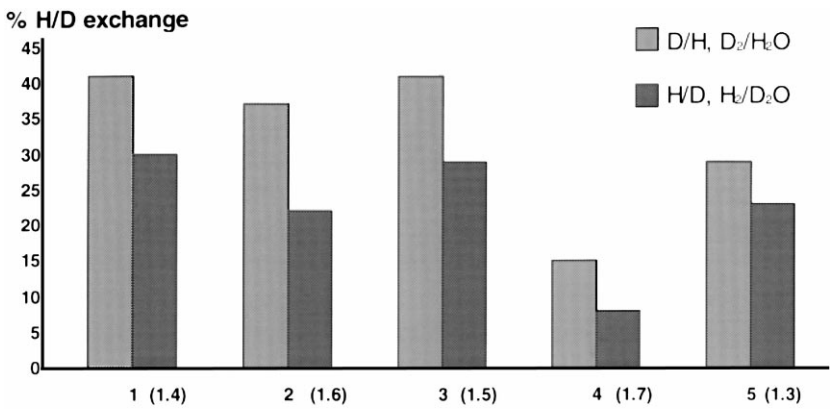



Fig. 1. Comparison of the H/D exchange within the $H_2O/D_2$ and $D_2O/H_2$ systems during the hydrogenation of methyl (*Z*)-α-acetamidocinnamate in the presence of different amphiphiles.

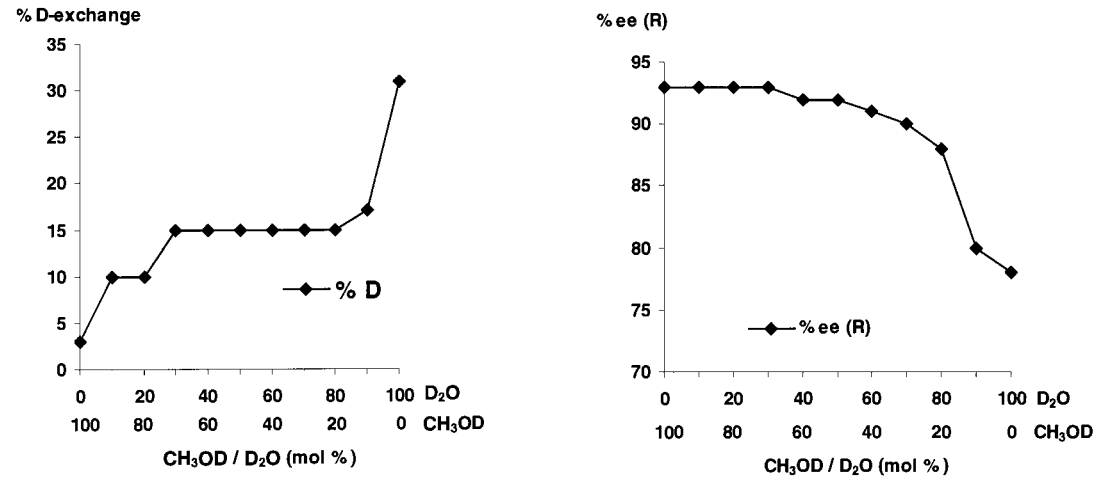



Fig. 2. CH/CD exchange and enantioselectivity with mixtures of $CH_3OD/D_2O$ during the hydrogenation of methyl (*Z*)-α-acetamidocinnamate.

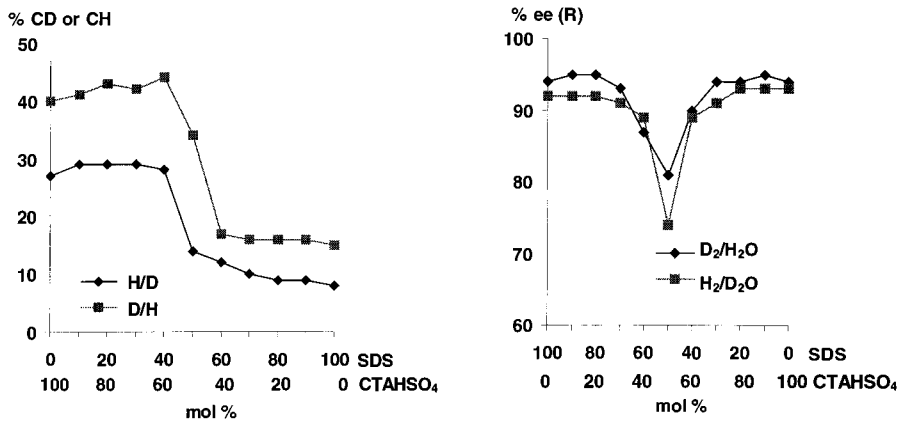



Fig. 3. Influence of SDS–$CTAHSO_4$ mixtures on the H/D exchange and the enantioselectivity during the hydrogenation or deuteration of methyl (*Z*)-α-acetamidocinnamate in $D_2O$ or $H_2O$.

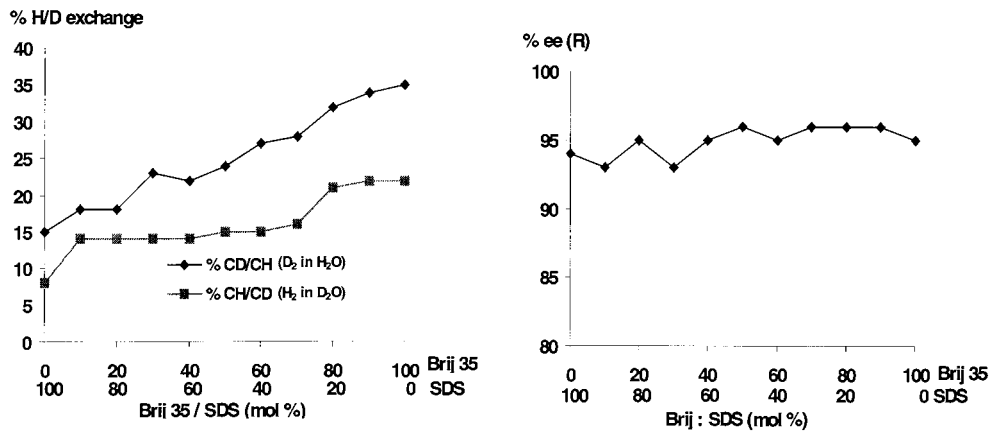



Fig. 4. Influence of SDS–Brij 35 mixtures on the H/D exchange and the enantioselectivity during the hydrogenation or deuteration of methyl (*Z*)-α-acetamidocinnamate in $D_2O$ or $H_2O$.

In order to be sure that we really had a mixed micelle system, we used different mixtures of SDS (CMC $8.1 \times 10^{-3}$ mol $l^{-1}$ at 25°C in water) and Brij 35 (polyoxyethylene(23) dodecyl ether, $C_{12}E_{23}$; CMC $6 \times 10^{-5}$ mol $l^{-1}$ at 25°C in water) [18]. As a rule the composition of the micelle depends on the ratio $CMC_2/CMC_1$, and it is to be expected that Brij 35 is enriched in micelles [19]. No precipitation was observed during

the mixing of the surfactants. As shown in Fig. 4, both enantioselectivity and CH/CD exchange in the hydrogenation are dependent on the surfactants added.

As expected, the enantioselectivity is rather constant: between 92 and 94% e.e., similar to values observed in micelles of pure Brij 35 or pure SDS [20]. In contrast to this, the CH/CD exchange in $D_2O$ drops from pure Brij 35 micelles (22% CD in α-position) to pure SDS micelles (8% CD in α-position), and stays practically constant between 30 and 90 mol% of SDS. There is a great similarity to the exchange in $CH_3OD/D_2O$ mixtures (Fig. 2), but the distinction between these is the deviation of the micelle composition from the stoichiometry of the mixture. In the beginning the micelles contain only very small amounts of SDS and the ratio is almost constant over a large range. Only in the last 10 mol% of added SDS is a significant decrease of nearly 6% CH/CD exchange observed. The non-linearity could be a result of the non-linear micelle composition.

Moreover, we have to expect a mixture of mixed micelles and a few SDS micelles in the region of a high mole fractions of SDS. The results in mixed micelles show a sort of solvent effect in the environment of amphiphiles, but a specific interaction between the amphiphilic sulfate anion and rhodium complex is not clear [21].

To check the connection between micelle formation and CH/CD exchange we used sodium decyl sulfate (SDeS) as the amphiphile, which has a relatively high CMC ($3.3 \times 10^{-2}$ mol $l^{-1}$ at 25°C in water [18]). The results are presented in Fig. 5.

Activity and enantioselectivity show a significant change between Rh/SDeS ratios of 1:20 and 1:50 (in the region of the CMC). In comparison with that the CH/CD exchange is much less variable, and we found a clear inhibition (cf. entries 1 and 2 in Table 1) below the CMC, indicating non-micellar specific interactions of the sulfate with the catalyst [22].

Taking all the evidence into account, we can develop the following mechanistic argument. On the basis of the hydrogenation mechanism developed by Halpern [2], and with respect to the results submitted by Sinou and co-workers [10] obtained in $D_2O$ using a two-phase system, we conclude that the H/D exchange occurs in the rhodium–alkyl intermediate (**4**) (Scheme 2) between the Rh–H bond and the coordinated $D_2O$ (S).

The inhibition of the exchange could be caused by competition between the coordination of $D_2O$ and the alkyl sulfate anion. The effect is optimal with a long-chain sulfate. The transfer of H or D from Rh–H(D) to the σ-bound substrate is most likely to be responsible for the isotope effect.

## 3. Conclusions

Amphiphiles influence the asymmetric hydrogenation of dehydroamino acid derivatives in an aqueous medium by enhancing activity and enantioselectivity. The effect is observed only above the CMC and seems to be typical for a reaction within a micelle. By changing the aqueous phase to $D_2O$ the α-hydrogen was partially exchanged for deuterium. This incorporation of deuterium is also influenced by amphiphiles, and, indeed, below the CMC. Anionic amphiphiles, like sodium alkyl sulfates or sodium alkanesulfonates in particular, inhibit the exchange significantly. Additionally, investigations into systems with amphiphile mixtures show clearly that a non-micellar reaction is responsible for the exchange. The step at which exchange and competition in coordination between the isotopic solvent and the sulfate- or sulfonate-containing amphiphile take place has been proposed within the Halpern mechanism. Amphiphiles exert a stabilizing effect on the catalytic system, and in their absence the exchange of H/D is high, but often there is a precipitation of rhodium.

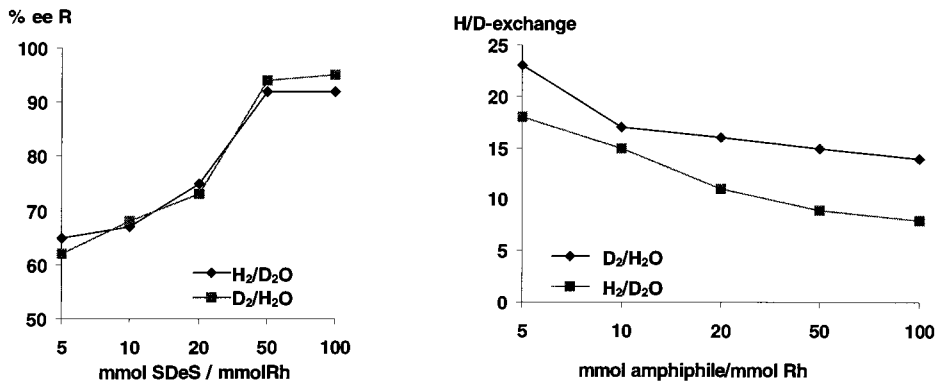
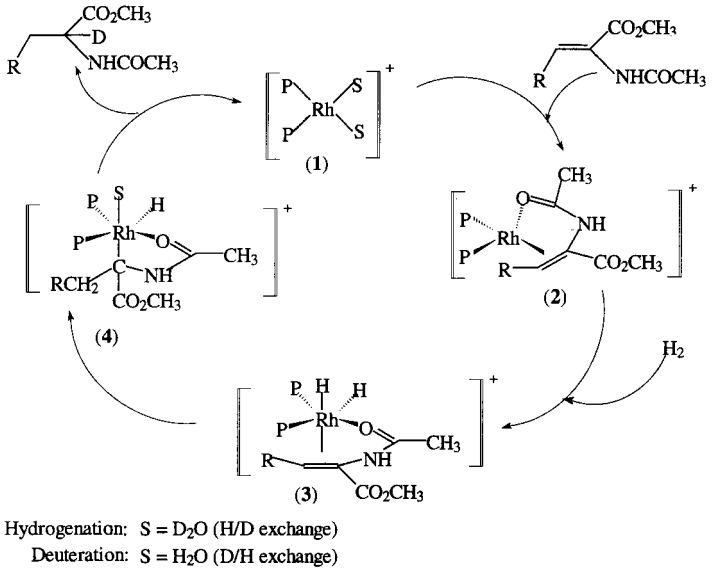



Fig. 5. Influence of different SDeS concentrations on the enantioselectivity and the H/D or the D/H exchange during the hydrogenation or deuteration of methyl (*Z*)-α-acetamidocinnamate in $D_2O$ or $H_2O$.




Scheme 2. Mechanism of the hydrogenation (deuteration) with the H/D exchange within step (4).

## 4. Experimental

### 4.1. General procedures

NMR spectra were recorded on a Bruker AC 250 instrument. Chemical shifts of $^1H$ are reported in parts per million and referenced to $Me_4Si$ as standard. The mass spectra were recorded on an AMD 402 instrument (Fa. Intectra).

The e.e. was determined by GLC on a Hewlett–Packard chromatograph 5880 A equipped with a 10 m capillary column (column ID: 0.2 mm), fused silica, XE-60 L-valine-*tert* butylamide (FID, split 1:60, 150°C).

All detergents and BPPM were purchased from commercial sources and used as obtained. Tween and sulfobetaines were obtained from Sigma GmbH, BPPM from Merck, $CTAHSO_4$, SDS and Brij-compounds from Fluka. The complexes $[Rh(cod)_2]BF_4$ [23], $[Rh(cod)(bppm)]BF_4$ [24,25] and methyl (*Z*)-α-acetamidocinnamate [26,27] were prepared in accordance with the literature.

### 4.2. General procedure for hydrogenation (deuteration)

Hydrogenation was performed by an isobaric method at 25°C under air-free conditions in thermostatically controlled apparatus [20]. A suspension of 1 mmol methyl (*Z*)-α-acetamidocinnamate, 0.01 mmol $[Rh(cod)_2]BF_4$, 0.01 mmol of the phosphine ligand and 0.2 mmol surfactant in 15 ml of deaerated $D_2O$ was stirred for 15 min under argon in a double-walled hydrogenation flask. The stirring was stopped and the argon replaced by hydrogen at atmospheric pressure; the hydrogenation was started by stirring. The reaction was followed volumetrically. The time necessary to consume half of the theoretical amount of hydrogen (half-life of the reaction) was taken as a measure for the activity. After finishing the experiment, the mixture was extracted with 5 ml of chloroform. The deuteration was performed by exactly the same method, but the system $D_2/H_2O$ was used instead of $H_2/D_2O$. The e.e. of the product was determined by GLC as described above.

The H/D exchange was estimated quantitatively by comparison of the $^1H$-NMR signals of the hydrogenation product and checked by MS (CI; parent peak). All results are in good accordance.

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