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# Nonlinear phenomenon in heterogeneous enantioselective catalysis

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## Abstract

The nonlinear behavior of modifier mixtures has been studied with the use of the enantioselective hydrogenation of ketopantolactone to pantolactone as an industrially important model reaction. A 5 wt% Pt/$Al_2O_3$ catalyst was modified by pairs of enantiomers, diastereomers, and chemically different chiral compounds possessing the same or different anchoring moieties (i.e., the part of the molecule responsible for the strong adsorption on the metal surface). The linear correlation observed with mixtures of the two enantiomers ($R,R$)- and ($S,S$)-pantoyl-naphthylethylamine is in agreement with the generally accepted 1:1 type reactant:modifier interaction. A strong nonlinear phenomenon was observed only when the anchoring moieties of the two modifiers were different. The dramatic nonlinearity induced by the addition of cinchonidine to ($S$)-naphthylethylamine or ($S,S$)-pantoyl-naphthylethylamine is traced to the different adsorption behaviors of the quinoline and naphthalene fragments of the modifiers on Pt. In an extreme case, ($R$)-pantolactone was produced with 26.5% enantiomeric excess (ee) with the use of a mixture containing only 0.5 mol% cinchonidine, although the ($S$)-product was obtained with 74% ee when ($S,S$)-pantoyl-naphthylethylamine was applied alone as a modifier. The results indicate that (i) 1:1 type interactions determine the enantioselectivity, and ordered two-dimensional chiral arrays do not play a role; (ii) the nonlinear phenomenon is traced mainly to the different adsorption strengths of the modifiers, although there is no general correlation between the adsorption strength and the effectiveness of the modifiers used alone; (iii) only traces of a strongly adsorbing impurity ($\ll$ 1 mol%) can significantly distort the ee, but large amounts ($\approx$ 50 mol%) of a weakly adsorbing impurity may have a negligible influence on the enantioselection.

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*Keywords:* Asymmetric hydrogenation; Platinum; Naphthylethylamine derivatives; Cinchonidine; Nonlinear effect

## 1. Introduction

The nonlinear effect in asymmetric catalysis has been a topic of great interest in the past two decades. According to the classical assumption, the enantiomeric excess (ee) of the product is proportional to the ee of the chiral auxiliary or ligand. A requirement for this assumption is that the two enantiomers of the auxiliary provide the same rate of the asymmetric reaction but give the opposite enantiomers of the product in excess. Kagan demonstrated for the first time the nonlinear behavior of enantiomerically impure chiral auxiliaries [1]. The mechanistic principles and practical consequences of the phenomenon in homogeneous catalysis have been thoroughly discussed, and numerous examples in various asymmetric reactions have been collected [2–7]. The concept has been extended to pseudo-enantiomeric or diastereomeric auxiliaries and to two chemically different ligands that give products of opposite configuration [8–10].

In heterogeneous enantioselective catalysis only the latter "extended" nonlinear effect has been studied so far. Examples include the Pt-catalyzed hydrogenation of activated ketones [11–16] and the C=C bond of an alkenone [17], an alkenoic acid [18], and a pyrone [14,19]. The nonlinear behavior of mixtures of two diastereomers or two completely different chiral modifiers has been attributed to their different adsorption strengths [11] and geometries [13] on Pt or Pd. It is not clear yet whether there is any nonlinearity when two enantiomers are used as the source of chirality and whether modifier–modifier interactions on the metal surface contribute to the observed nonlinearity.

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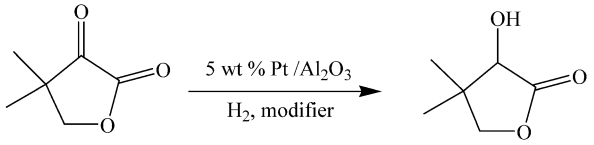

Scheme 1. Enantioselective hydrogenation of ketopantolactone to pantolactone over chirally modified platinum.

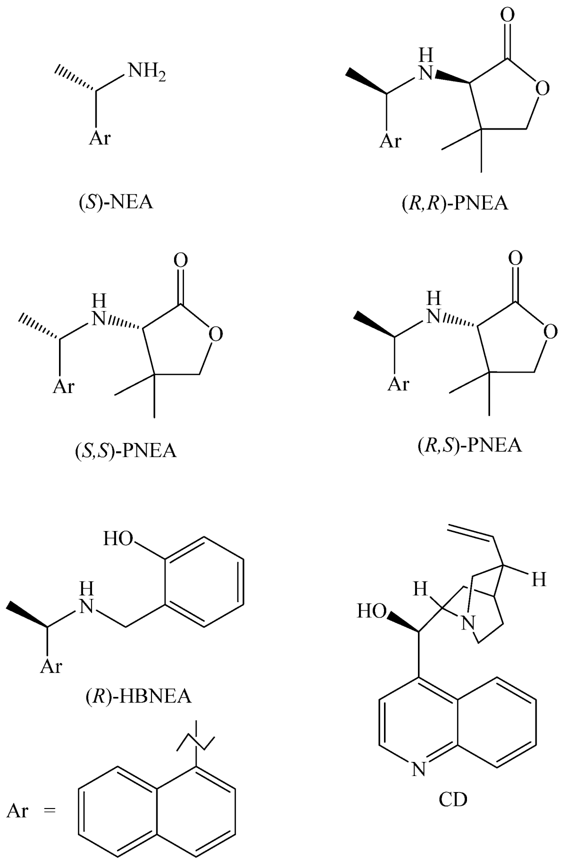

Fig. 1. The chiral modifiers used in this study.

In the following, the nonlinear behavior of modifier mixtures in heterogeneous catalysis are referred to as a “nonlinear phenomenon” to clearly separate it from the nonlinear effect (NLE) in homogeneous catalysis.

Here we present a systematic study of the nonlinear phenomenon, including the application of mixtures of enantiomers, diastereomers, and chemically different chiral compounds possessing the same or different “anchoring moiety” (essentially the aromatic ring via which the molecule is anchored to the metal surface). Hydrogenation of ketopantolactone to pantolactone over Pt/Al$_2$O$_3$ has been used as a model reaction (Scheme 1); the modifiers applied are shown in Fig. 1. The reaction is of industrial relevance, since ($R$)-pantolactone is an intermediate in the synthesis of pantothenic acid (vitamin B family) and a constituent of coenzyme A. Various soluble chiral Rh and Ru complexes afford up to 98.7% ee to ($R$)-pantolactone [20–25]. In heterogeneous catalysis Pt/Al$_2$O$_3$ modified by cinchonidine (CD) is the best choice [26–29], giving 91.6% ee under high-pressure conditions [30]. Other modifiers of Pt, such as the ether derivatives of CD [15], 1-naphthyl-1,2-ethanediol [31], and ($R$)-1-(1-naphthyl)ethylamine and its N-functionalized derivatives [32], are less effective, although at low pressures pantoyl-naphthylethylamine (PNEA) outperforms CD.

## 2. Experimental

### 2.1. Materials

Ketopantolactone (> 99%; Roche), cinchonidine (CD; Fluka), and (–)-($S$)-1-(1-naphthyl)ethylamine (NEA, 99%; Acros) were used as received. Toluene was dried and stored over activated molecular sieves. ($1'R,2R$)-, ($1'R,2S$)-, and ($1'S,2S$)-$N$-[1′-(1-naphthyl)ethyl]-2-amino-3,3-dimethyl-$\gamma$-butyrolacton (PNEA, Fig. 1) and (–)-($1R$)-$N$-(2-hydroxybenzyl)-1-(1-naphthyl)ethylamine (HBNEA, Fig. 1) were synthesized by known procedures [32]. Their structure and purity (> 99%) were confirmed by NMR, HPLC, and MS. The NMR spectra were recorded on a Bruker Avance 500 spectrometer.

### 2.2. Catalytic hydrogenation of ketopantolactone

The 5 wt% Pt/Al$_2$O$_3$ catalyst (Engelhard 4759) was prereduced before use at 673 K for 1 h in flowing hydrogen and cooled to room temperature under flowing hydrogen for 30 min. After this pretreatment the metal dispersion was 0.33, as determined by TEM. The catalyst was first brought into contact with the solvent, which contained the modifier(s). After a 5-min preadsorption period, the reaction was started by introduction of the reactant.

Two different reactors were used. The reactions under pressure were carried out in a multiple reactor system (Argonaut Technologies). The eight small mechanically stirred ($n = 1000\ \text{min}^{-1}$) autoclaves were equipped with 10-ml glass liners and Teflon caps to avoid contact with the metal surface. The pressure was held at a constant value by computerized constant-volume/constant-pressure equipment (Büchi BPC 9901). The standard reaction conditions were as follows: 10 mg prereduced catalyst, 236 mg ketopantolactone, 6.8 µmol modifier (or modifier mixture), 5 ml solvent, 8 bar, room temperature, and 1.5–2 h reaction time.

The reactions at atmospheric pressure were carried out in a magnetically stirred ($n = 1250\ \text{min}^{-1}$) 100-ml glass reactor. In a standard procedure, 10 mg catalyst was prereduced in 5 ml solvent in flowing H$_2$ for 5 min, at 1 bar and room temperature. Then 3.4 µmol of modifier in 1 ml solvent was added. After a 5-min preadsorption period the reaction was started by the introduction of 236 mg ketopantolactone in 4 ml solvent. After 4 min 3.4 µmol of another modifier was added.

The enantiomeric excess, (ee) $= 100 \times (|R - S|)/(R + S)$, was determined at full conversion with a HP 6890 gas chromatograph and a Chirasil-DEX CB (Chrompack

7502, 25 m × 0.25 mm × 250 nm) capillary column. No product other than pantolactone could be detected. The estimated standard deviation of the determination of ee was ±0.5%. The differential ee was calculated as $\Delta\text{ee} = (\text{ee}_1 y_1 - \text{ee}_2 y_2)/(y_1 - y_2)$, where $y$ represents the yield to the hydrogenation product, and index 2 refers to a sample subsequent to sample 1.

The average reaction rate was calculated from the conversion in 25–30 min to minimize the distortion by the initial transient period in the autoclave.

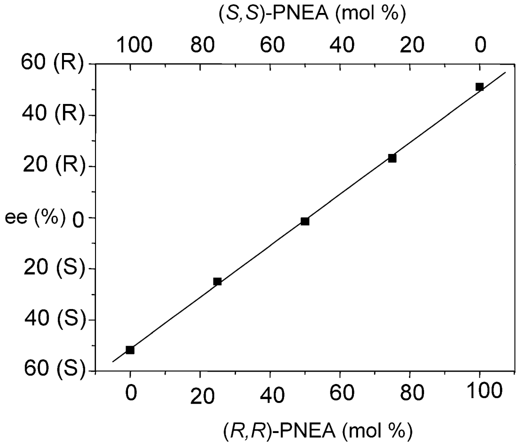

Fig. 2. Hydrogenation of ketopantolactone in 1,1,1-trifluorotoluene over $Pt/Al_2O_3$ modified by mixtures of $(R,R)$- and $(S,S)$-PNEA.

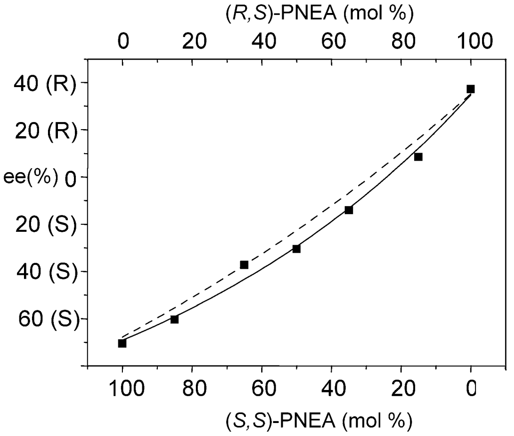

Fig. 3. Hydrogenation of ketopantolactone in acetic acid over $Pt/Al_2O_3$ modified by $(S,S)$- and $(R,S)$-PNEA. The dashed line indicates the ee calculated for an ideal behaviour of the modifier mixture.

## 3. Results

In the hydrogenation of ketopantolactone, ($R$)-pantolactone is formed in excess when Pt is modified by CD [27], ($R$)-NEA, ($R$)-HBNEA, and ($R,R$)- or ($R,S$)-PNEA [32], whereas ($S$)-pantolactone is the major enantiomer in the presence of ($S$)-NEA and ($S,S$)-PNEA [32]. In the following, the nonlinear phenomenon was studied with the use of mixtures of two modifiers that alone give the opposite enantiomers in excess.

### 3.1. Nonlinear phenomenon with modifier mixtures

At first, mixtures of two enantiomers of PNEA were applied while the total amount of modifiers was kept constant (Fig. 2). In 1,1,1-trifluorotoluene solvent, ($R$)- and ($S$)-pantolactone were produced with 51.1 and 51.7% ee in the presence of ($R,R$)- and ($S,S$)-PNEA, respectively. Considering the standard deviation of the analytical method, the difference between the two values is insignificant. The conversions achieved in 25 min (73.0 and 72.2%) are also considered to be identical. Similarly, only a negligible deviation from the linear correlation in enantioselectivity was observed in the whole concentration range. This ideal behavior was also observed in toluene, but the enantioselectivities were much smaller; the ee varied in the range of 11% for ($R$)- to 11% for ($S$)-pantolactone (not shown).

A small but significant deviation from the ideal behavior was obtained when a mixture of two diastereomers was applied (Fig. 3). The reactions in the presence of ($S,S$)- and ($R,S$)-PNEA alone were characterized by considerably different ees and average reaction rates (3.3 and 2.6 mmol $h^{-1}$, respectively), a commonly observed situation in various reactions when Pt or Pd is modified by two diastereomers, such as cinchonidine and cinchonine [18,33–38]. For the modifier mixtures the theoretical or expected ee (dashed line) was calculated with the assumption that the molar ratios of the modifiers in solution and on the metal surface are identical, they do not interact with each other, and the reaction rates with each modifier are the same as the reaction rates achieved with the modifiers alone. Fig. 3 demonstrates that the two diastereomers of PNEA do not behave ideally, although the deviation is minor. For example, the equimolar mixture of the diastereomers gave 30.6% ee for ($S$)-pantolactone instead of the calculated 21.6% ee (i.e., 9% deviation from the linear behavior).

Next, two chemically different modifiers, ($S$)-NEA and its N-hydroxybenzylated derivative, ($R$)-HBNEA, were mixed (Fig. 4). Here the nonlinearity was slightly more pronounced and ($S$)-pantolactone was produced, with 0.7% ee, for a mixture containing only 35% ($S$)-NEA, although the calculated ee for this modifier mixture was 17.5% for ($R$)-pantolactone. With equimolar amounts of modifiers, the deviation from the theoretical value was close to 12%. The reaction with ($S$)-NEA was faster by 10% than that in the presence of ($R$)-HBNEA. It is very probable that NEA and its N-substituted derivatives adsorb to Pt via the naphthalene ring [32,39–42], in a manner analogous to that of the adsorption of cinchonidine via the quinoline ring lying nearly parallel to the Pt surface [43–47]. Nevertheless, a contribution of the hydroxybenzyl fragment of HBNEA to the adsorption process cannot be excluded. Interestingly, deviation from the linear behavior of the modifier mixture suggests a

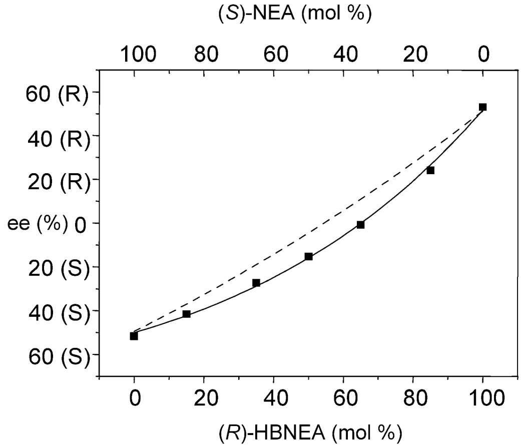

Fig. 4. Hydrogenation of ketopantolactone in acetic acid over Pt/$Al_2O_3$ modified by (*R*)-HBNEA–(*S*)-NEA mixtures. The dashed line indicates the calculated ee.

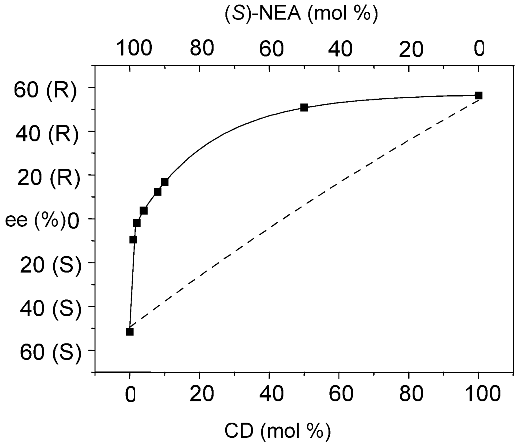

Fig. 5. Nonlinear behaviour of the CD + (*S*)-NEA mixture in the hydrogenation of ketopantolactone over Pt/$Al_2O_3$ in acetic acid. The dashed line indicates the calculated ee.

greater than proportional contribution of (*S*)-NEA to enantioselection.

Finally, the reaction was carried out with modifiers that were chemically different compounds, and the anchoring moieties were different. Figs. 5 and 6 show the nonlinear behavior of CD + (*S*)-NEA and CD + (*S*,*S*)-PNEA mixtures, respectively. Clearly, in both cases the performance of modifier mixtures deviates remarkably from the calculated linear correlation. More (*R*)-pantolactone than expected was always formed; that is, CD governed the enantioselection, although the reaction rate with CD (3.2 $\text{mmol h}^{-1}$) was only slightly higher than the rate measured in the presence of (*S*)-NEA (3.0 $\text{mmol h}^{-1}$) or (*S*,*S*)-PNEA (3.1 $\text{mmol h}^{-1}$). For example, (*R*)-pantolactone was produced with 3.7% ee by a CD + (*S*)-NEA mixture containing only 4% CD (Fig. 5). The nonlinearity was the greatest in the CD + (*S*,*S*)-PNEA system: the (*R*)-product formed with 26.5% ee with a modifier mixture containing only 0.5% CD (Fig. 6). A similar striking nonlinear phenomenon was found recently when cinchonine and (*R*,*R*)-PNEA were used as modifiers [32].

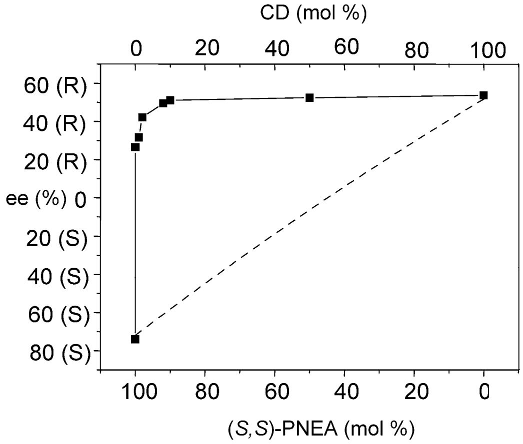

Fig. 6. Nonlinear behaviour of the CD + (*S*,*S*)-PNEA mixture in the hydrogenation of ketopantolactone over Pt/$Al_2O_3$ in acetic acid. The dashed line indicates the ee calculated for an ideal behaviour of the modifier mixture.

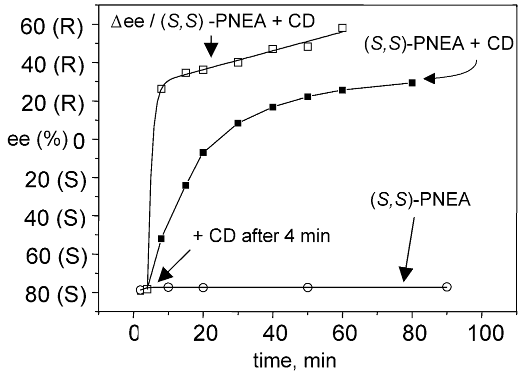

Fig. 7. Transient behaviour of ketopantolactone hydrogenation over Pt/$Al_2O_3$ in acetic acid, at 1 bar. An equimolar amount of CD was added after 4 min to the reaction mixture containing (*S*,*S*)-PNEA.

### *3.2. Transient behavior of modifier mixtures*

We showed earlier that a transient method offers a better visualization of the competition between two modifiers [13,14,19]. In this procedure the hydrogenation reaction is started in the presence of only one modifier, and after a short time period (at low conversion) the second modifier is injected into the slurry. Fig. 7 presents the experiment with CD and (*S*,*S*)-PNEA. Under the conditions applied here, in acetic acid (*S*)-pantolactone was produced with 78% ee in the presence of (*S*,*S*)-PNEA, and (*R*)-pantolactone formed with 53% ee when CD was applied alone as a modifier of Pt (not shown for the sake of clarity). When the reaction with (*S*,*S*)-PNEA was repeated and after 4 min an equal amount of CD was injected into the reactor, the ee for (*S*)-pantolactone decreased rapidly, and shortly thereafter the opposite enantiomer was produced in excess. The transient behavior is even more striking when the calculated differential ee (Δee) is considered. Apparently, CD rapidly replaced (*S*,*S*)-PNEA on the Pt surface and the alkaloid governed the enantioselection. In the control experiment (not shown) the reaction was started with CD, and (*S*,*S*)-PNEA was added after 4 min, but the latter modifier had only negligible influence on the ee ($< 1\%$).

## 4. Discussion

For the Pt-catalyzed enantioselective hydrogenation of activated ketones, all existing mechanistic models assume 1:1 type interactions between modifier and reactant during hydrogen uptake on the metal surface (although there is a lively debate on the true nature of interactions leading to enantioselection; for a recent review see [48]). If these models are valid, no deviation from the linear behavior of two enantiomers of a chiral modifier is feasible, in agreement with the interpretation of the nonlinear effect in homogeneous asymmetric catalysis [5,6]. Note, however, that the first model developed for the enantioselective hydrogenation of pyruvate esters assumed the formation of an ordered array of CD on the Pt surface as the source of chiral information (the "template" model [49]). Later the proposal was withdrawn [50] because of a contradiction of experimental observations indicating a 1:1 type interaction between CD and the $\alpha$-ketoester. Interestingly, recent surface science studies revealed the formation of highly ordered, two-dimensional chiral domains on extended single crystal surfaces [51–55]. The linear correlation observed with mixtures of the two enantiomers of PNEA (Fig. 2) confirms our expectation and provides indirect evidence against the importance of ordered chiral arrays in practical catalysis on Pt nanoparticles. Note that a recent STM study of cinchonidine adsorption on Pt(111) also excludes the formation of ordered arrays [56].

There are several explanations in the literature for the nonlinear behavior of diastereomers or chemically different chiral compounds used as modifiers. Wells and coworkers suggested that the stronger adsorption of cinchonidine and quinine on Pt was the reason for the small nonlinearity observed in the hydrogenation of methyl pyruvate with cinchonidine–cinchonine and quinine–quinidine alkaloid mixtures, respectively [11]. We proposed that the different adsorption strengths of cinchona alkaloids may result in different adsorption geometries of the molecules anchored via the quinoline moiety [13]. A perpendicular or strongly tilted position of the aromatic ring may hinder the modifier–reactant interaction, leading to enantioselection, and may be the reason for the prominent nonlinearity observed with cinchonidine–quinidine mixtures. On the basis of adsorption studies by UV–vis spectroscopy, this effect seemed to be more influential than that of the different surface concentrations. A third possible interpretation is connected with the different chemical stability of the modifiers [12]. The rapid saturation of the aromatic ring under high hydrogen pressure leads to weaker adsorption and a loss of enantiodifferentiating ability of the modifier. The different resistance of the quinoline and naphthalene rings against hydrogenation may contribute to the generally observed superiority of cinchona alkaloids. Finally, it was speculated [13] that modifier–modifier interactions may also contribute (to a small extent) to the nonlinear phenomenon, but no experimental evidence has been found yet.

Next we address the results presented in Figs. 2–7. It is not possible yet to provide an unambiguous interpretation of the minor nonlinearity detected with the diastereomers $(S,S)$- and $(R,S)$-PNEA (Fig. 3). The nonlinearity increased when mixtures of $(S)$-NEA and its N-hydroxybenzylated derivative $(R)$-HBNEA were applied (Fig. 4). A plausible explanation for the enhancement is the weaker adsorption of $(R)$-HBNEA due to some steric hindrance by the additional functional group. An analogy is the weaker adsorption of $O$-phenyl-cinchonidine relative to cinchonidine and the resulting striking nonlinear behavior observed in ketopantolactone hydrogenation [15]. Another explanation based on modifier–modifier interactions involving the weakly acidic phenolic OH function is also feasible.

Considerable nonlinear behavior was observed only when the two modifiers possessed chemically different anchoring moieties (Figs. 5–7). In these reactions cinchonidine always governed the enantioselection, presumably because of the stronger adsorption of the quinoline ring of cinchonidine relative to the naphthalene ring of the other two modifiers. Since the reactions were carried out at low pressure (8 bar), hydrogenation of the naphthalene rings of NEA and PNEA is expected to be negligible [32]. A comparison of Figs. 5 and 6 reveals that again the primary amine $(S)$-NEA adsorbed more strongly than the N-functionalized derivative $(S,S)$-PNEA, although the latter molecule alone is a more efficient chiral modifier of the reaction than $(S)$-NEA. It is also interesting that under the conditions applied, $(S)$-PNEA alone afforded higher ee than cinchonidine, which adsorbs far more strongly on Pt. Obviously, there is no direct correlation between the adsorption strength of the modifiers and their effectiveness in enantioselection, even though a strong adsorption to the metal surface is a necessary requirement for enantio-differentiation [48].

## 5. Conclusions

No deviation from the ideal, linear behavior was detected in the enantioselective hydrogenation of ketopantolactone over $Pt/Al_2O_3$ modified by mixtures of the two enantiomers of pantoyl-naphthylethylamine ($(S,S)$- and $(R,R)$-PNEA). This observation may be considered indirect evidence for the mechanistic models assuming 1:1 type modifier: reactant interactions and against the importance of possible ordered, two-dimensional chiral domains in enantioselective catalysis on small metal particles [57].

Only the use of mixtures of chemically different chiral modifiers resulted in a considerable nonlinear phenomenon. The origin of the sometimes striking nonlinearity is traced to the different adsorption strengths of the chiral molecules.

All of the experimental evidence gathered so far indicates that measuring the nonlinear behavior of modifier mixtures is at present the only way to estimate the (relative) adsorption strength of chiral modifiers on metal surfaces under the reaction conditions. Another consequence of the nonlinear phenomenon is that even trace amounts ($\ll 1\%$) of a strongly adsorbing impurity in the modifier can significantly distort the enantioselectivity and lead to a false conclusion in a mechanistic study. This is the case, for example, when a weakly adsorbing derivative of cinchonidine is not separated carefully from the original alkaloid. The positive side of the nonlinear phenomenon is that even large amounts of impurities in the modifier may not diminish the enantioselectivity if the other chiral modifier(s) adsorb sufficiently more weakly than the major component. This fortunate situation allows us to achieve better than 90% ee with cinchonidine-modified Pt, although the commercially available CD contains considerable amounts of quinidine, and the two alkaloids afford the opposite enantiomers in excess [14].

## Acknowledgment

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