

Theoretical studies of enantiospecific adsorption on surfaces with chiral patterns of active sites

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Adsorption of a racemic mixture of enantiomers of 1,2-dimethylcyclopropane on a patterned chiral surface is studied using Grand Canonical Monte Carlo technique. The adsorbing surface is assumed to be completely flat and composed of two types of sites one of which is more strongly adsorbing (active sites) than the other (inert sites). A key point of the model is a special spatial distribution of the active sites leading to enantioselectivity towards one of the enantiomers. In particular, we study the case when the surface as well as its mirror image are exposed to the racemic mixture. The obtained results which include adsorption isotherms and the corresponding selectivities suggest that even flat surfaces with chiral patterns of active sites can lead to effective enantioseparation.

1. INTRODUCTION

Separation of optical isomers by adsorptive processes is one of the most powerful methods in the fabrication of enantiopure chemicals and pharmaceuticals. A central position in this field holds liquid chromatography which utilizes chiral stationary phases (CSPs) composed of a silica support with chiral ligands capable of selective recognition of the complementary enantiomer [1]. However, it has been observed recently growing interest in chiral surfaces which are created using single crystal planes [2]. Those chiral surfaces can be obtained in different ways, for example by cleavage of achiral bulk structures such as metals, templating surfaces with organic modifiers or exposing of surfaces of naturally chiral crystals. In all of the cases mentioned above, the resulting surface has a unique structure which is not superimposable with its mirror image and thus it is chiral. Because of the chirality, the surface interacts

more strongly with those molecules which are complementary to the surface, that is they fit chiral nanostructures created on the surface. This property, for example, makes the surface selective towards one of enantiomers adsorbed from a racemic mixture. Indeed, both experimental [3] and theoretical [4] studies confirm that nanostructured chiral surfaces can be used for the separation of enantiomers.

The chiral surfaces obtained by the methods mentioned above are in general rough (steps, kinks, etc.) or they have extra molecular structures bonded to initially flat surface. However, as we demonstrate in this contribution existence of a particular 3D nanostructure on the surface is not necessary condition for enantioselectivity. Namely, in this work we study the adsorption of a equimolar mixture of enantiomers of 1,2-dimethylcyclopropane on a completely flat surface with a special chiral distribution of active sites. The sites forming the chiral pattern can be treated, for example, as foreign atoms on an exposed surface of a hypothetical metallic alloy crystal.

2. SIMULATION

In order to make the surface enantioselective towards one of the enantiomers the active sites were distributed in such a way that the chosen enantiomer adsorbs more strongly than the other. This distribution is shown in Figure 1 for both S and R isomer.

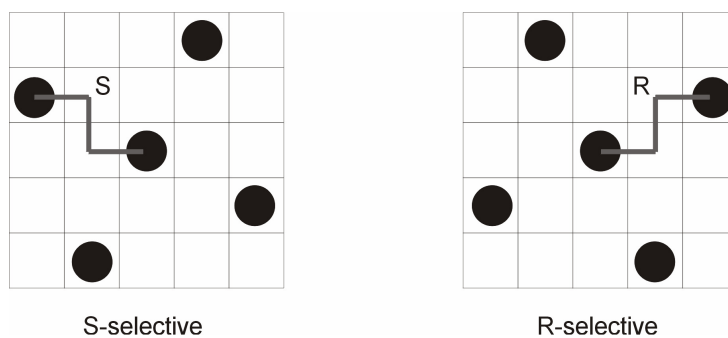


Fig. 1. The arrangements of active sites (filled circles) on a square lattice leading to enantioselective adsorption of S enantiomer – left panel and R enantiomer – right panel.

In the model proposed here a key point is the lack of steric requirement for a particular enantiomer to be adsorbed as it is usually assumed in literature [5]. In other words, all the adsorption sites are equally accessible for both enantiomers and the deciding factor in their separation is a difference in the number of active

sites occupied by each of them. As seen in Figure 1 a molecule of R type can occupy two selective sites on the surface selective towards that enantiomer. This situation is, however, impossible in the case of S molecule adsorbed on R-selective surface. Here a single molecule can occupy at most one selective site. A similar conclusion refers also to a molecule of R type adsorbed on a S-selective surface. In consequence a surface composed of one of the patterns of active sites shown in Figure 1 can act as an adsorbent which is selective towards the corresponding enantiomer. Obviously, as one may expect, the resulting selectivity should be strongly influenced by the difference between the adsorption energies assigned to the selective and inert sites. To study this effect we performed computer simulations of the adsorption of the racemate for different values of both energies characterizing the surface.

The simulations were performed on a square lattice of a side $L = 50$. The active sites were arranged on the lattice according to the pattern shown in the left panel of Figure 1 (S-selective surface). In consequence the resulting lattice consisted of 10×10 building blocks shown in the figure. Regardless of the type of adsorbing molecules, it was assumed that the enantiomers are weakly interacting when adsorbed, that is intermolecular interactions were neglected as first approximation. Furthermore, the enantiomers were assumed to be rigid molecules composed of four segments. The carbon atom in the C-C-C ring which is not bonded with methylene groups was treated as non-interacting with the surface. Consequently, the enantiomers were allowed to adsorb in a fixed position which involves occupation of four adsorption sites as shown in Figure 1. The energy of interaction between an active site and a segment of the molecule (carbon atom) was characterized by ε_a while that between inert site and the segment by ε_i . The simulations were carried out using standard GCMC technique for adsorption on a lattice [6]. In the case of the racemic mixture considered here a fixed molar composition of the gas phase was set 1:1 such that partial absolute activity of each enantiomer was equal to 0.5λ with λ being the total absolute activity of the racemate. The fractional coverage of each enantiomer at a fixed λ was an average over 1000 independent runs. For each value of λ typically up to 2000 Monte Carlo steps (L^2 attempts of changing the system state) was performed. We would like to emphasize that the results presented here have preliminary character because they correspond to a relatively short equilibration time of the system, which makes the adsorbed phase far from equilibrium. Nevertheless, those results reflect interesting kinetic features of the enantioselective adsorption and thus we decided to describe them in more detail.

3. RESULTS AND DISCUSSION

Figure 2 shows the adsorption isotherms of enantiomers of 1,2-dimethylcyclopropane adsorbed on S-selective surface. The results presented in both panels correspond to $\varepsilon_i = 1$, but they were obtained for different values of ε_a . Namely, the data shown in the left panel were simulated for $\varepsilon_a = 2$ while those displayed in the right panel for $\varepsilon_a = 4$.

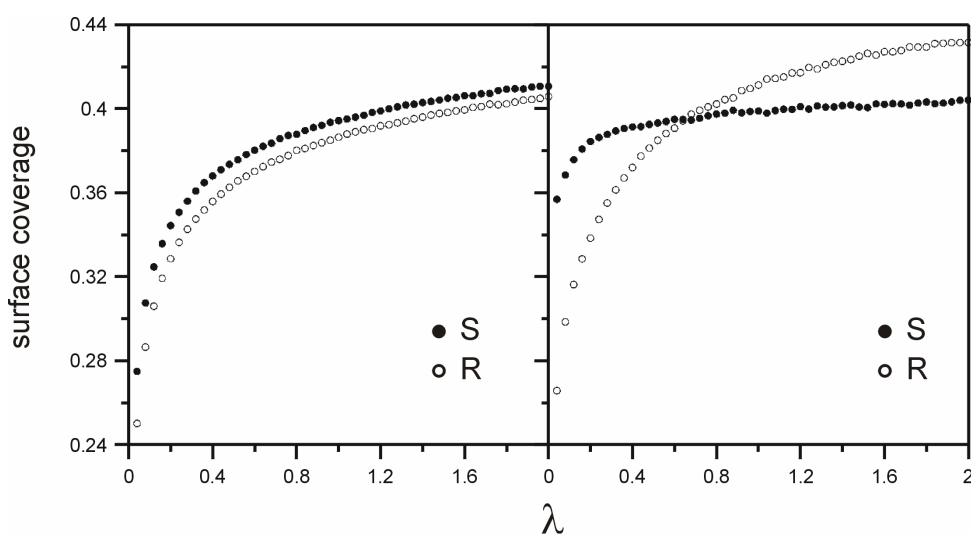


Fig. 2. The adsorption isotherms of enantiomers of 1,2-dimethylcyclopropane adsorbed on S-selective surface. The curves shown in the left panel correspond to $\varepsilon_a = 2$ while those shown in the right panel correspond to $\varepsilon_a = 4$.

As it is seen from Figure 2 the isotherms corresponding to R and S enantiomer display markedly different behaviour depending on the magnitude of the parameter ε_a . In the case of weaker interaction between the active site and a segment of the enantiomer ($\varepsilon_a = 2$) we can observe that R and S isotherms are of nearly the same shape with S isotherm being shifted upward compared to the other. Here, S enantiomer is preferably adsorbed from the racemate, regardless of the total absolute activity (pressure). A completely different surprising behaviour can be, however observed in the right panel. As it is seen in that panel, for sufficiently low values of λ (less than ~ 0.6) S enantiomer is much more strongly adsorbed than R enantiomer which is quite logical consequence taking into account increased strength of the active site – segment interaction ($\varepsilon_a = 4$).

Surprisingly, this trend reverses when λ exceeds ~ 0.6 . In particular, at this total absolute activity molar composition of the adsorbed phase is equal to that in the bulk phase. In other words, the surface loses its enantioselective properties. However, when λ further increases the surface becomes selective again but this time towards R enantiomer. To illustrate better the effects discussed above in Figure 3 we showed the selectivity defined as the ratio of S-surface coverage to R-surface coverage plotted against the total absolute activity.

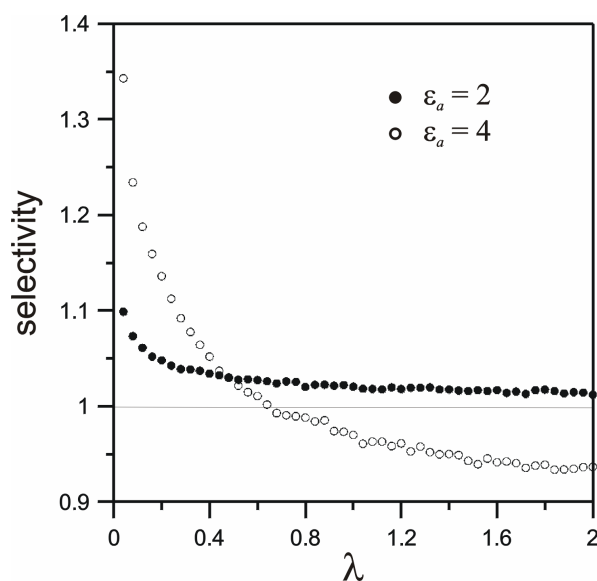


Fig. 3. The influence of the total absolute activity of the racemate on the selectivity defined as the ratio of surface coverages of S and R enantiomers.

As it is seen in Figure 3, the selectivity calculated for $\epsilon_a = 2$ initially drops rapidly for small total activities and next decreases gradually with increasing λ . In this case the curve closely approaches its limiting value equal to 1. On the other hand, the curve corresponding to $\epsilon_a = 4$ initially drops faster than that calculated for $\epsilon_a = 2$. Additionally, in this case the selectivity does not tend to 1 and it passes through that value being gradually smaller with increasing λ . The results presented above suggest that the selectivity of the surface designed to adsorb one enantiomer can be drastically influenced by changing the strength of the active site-molecule interaction by, for example, replacing foreign atoms in the alloy by atoms of a different metal. The surprising reversal of the adsorption trend exhibited by the system equilibrated within relatively short time indicates that enantioselective separations on chiral surface can show much richer

behaviour than observed usually in separations of gas or liquid mixtures. In this context, further experimental and theoretical studies are indispensable to clarify the picture sketched in this short contribution.

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