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Enantiospecific Wetting

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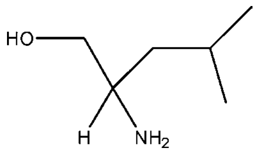
Abstract: Experiments have shown that enantiospecificity can be important in wetting. Measurements of droplet contact angles can be used to estimate the energy of enantiomeric discrimination.

The difference in the energies of interaction of enantiomers with a chiral object is a fundamental property of molecules that leads to enantiomeric selectivity in chemical reactions and has been much celebrated by both organic chemists and the biosphere. One particularly simple interaction is the wetting of a liquid by a solid. If both the solid and liquid are chiral, then the wetting must change if one of the solids or a component of the liquid is replaced by its enantiomer. However, to the best of our knowledge, there has never been a demonstration of chiral effects on wetting, and this point was recently raised by Stillinger in Faraday Discussion 146.[1] This communication demonstrates such differences in wetting for two enantiomers on a chiral solid, and also shows that the contact angle provides a route for calculating the difference in the energies of interaction for the two enantiomers, i.e., it provides a method for calculating the energy of chiral specificity.

The interaction between a chiral solid and a chiral liquid phase is the key step in the process of chiral chromatography that is widely used for the separation and characterization of chiral mixtures that are intermediates for enantiopure drugs. Some active areas of chiral selectivity at interfaces are briefly mentioned here. The groups of Gellman,[2−6] Sholl,[7,8] and others[9] have shown that certain high Miller index planes of metals are chiral and contain kink sites that demonstrate chiral selectivity. McKendry[10] and others[11,12] have recorded differences in surface forces with different enantiomers tethered to solids, and there are a number of studies of differences in adsorption measured for enantiomers by surface-selective techniques (e.g., see refs 13−15). Our group has also measured enantiomeric excess at interfaces using selectively deuterated adsorbates.[16]

Although differences in energy are assured in the interaction between two chiral materials, the extent of such differences, and thus the magnitude of the contact angle difference, depends on the difference in the interaction energies of the two enantiomers of the chiral liquid with the chiral solid (the energy of chiral discrimination). For this reason, we chose a chiral liquid that has four rather different chemical groups around a central carbon atom in order to provide the opportunity for larger energy differences between the enantiomers. Our choice was further refined by the need for the compound to be liquid at a convenient temperature. We chose leucinol (boiling point 199 °C), which has hydrogen, an alcohol, an amine, and a branched alkane around a central carbon atom (Scheme 1).

Scheme 1. Leucinol



To demonstrate chiral interactions with a solid, it is unnecessary for the bulk solid to have a chiral space group; it is sufficient that the surface is chiral, and a chiral film can simply be added to the surface of any solid. We prepared a chiral film on O_2-plasma-cleaned (2 min, 17 mW, 200 mTorr) silicon wafers (p-doped, obtained from Wafer World, FL) by heating the silinol-terminated silicon wafers to 120 °C under N_2 for 2.5 h while they were immersed in a chiral alcohol, using the method of Dion et al.[17] The wafers were rinsed in ethanol, water, and ethanol and then dried. For simplicity, we used leucinol (Sigma-Aldrich) for this procedure, ensuring that the liquid and solid had very similar character. Although this procedure was simple and effective, in retrospect it was not the ideal method for making chiral films because it used a large volume of a pure chiral reagent (~5 mL to cover a 1 cm^2 piece of wafer). The success of the grafting was confirmed using X-ray photoelectron spectroscopy (XPS), which showed (a) an increase in carbon content, (b) the presence of nitrogen, and (c) the presence of C−O bonds after the grafting.

Figure 1 shows photographs of the advancing contact angles of leucinol droplets on an (*S*)-leucinol-derivatized silicon wafer in hexadecane. It is clear that the advancing contact angle is greater for the (*S*)-leucinol liquid than for the (*R*)-leucinol liquid.

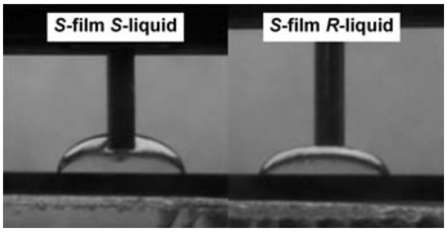


Figure 1. Leucinol droplets on an (*S*)-leucinol-modified silicon wafer in hexadecane. Advancing contact angles are shown [~85° for (*S*)-leucinol and ~74° for (*R*)-leucinol].

Before we could attribute this result to enantioselectivity, it was important to consider a number of control experiments. First, contact angles are quite sensitive to adsorption of small amounts of surface-active impurities, raising the possibility that the difference was due to a contaminant in one of the enantiomers in the liquid. We measured the surface tensions of the two liquids and found that they were the same ($\gamma = 29.0$ mJ m^{-2}), which is inconsistent with high levels of contamination. We also measured the contact angles of the same two liquids on an achiral surface: a silicon wafer that had been cleaned with oxygen plasma. The interactions of the two pure enantiomers with the achiral solid should be the same, but if the result in Figure 1 were due to an impurity, we would expect the angles to be different. The (*R*)-leucinol droplet had advancing angle, θ_A, of 35° and a receding angle, θ_{Rec}, of 15°, and the (*S*)-leucinol droplet had $\theta_A = 35°$ and $\theta_R = 17°$. The close similarity suggests that there was not a significant difference in the amounts of surface-active contaminant in the enantiomeric liquids.

Additional support for the idea that the difference in contact angle shown in Figure 1 arose from chiral interactions came from examining the four available combinations of optical isomerism produced by the two different surface-grafted molecules and the two different liquids (Figure 2). For convenience, we will use the nomenclature of naming the solid followed by the liquid (i.e., *SR* denotes the *S* solid and the *R* liquid). Figure 1 shows that on the *S* solid, $\theta_{SS} > \theta_{SR}$. Thus, we would expect that on the *R* solid, the mirror-image result (i.e., $\theta_{RR} > \theta_{RS}$) would also hold, and this is what we observed, as shown in Table 1. In addition, we would expect pairs of enantiomers to give the same result (i.e., $\theta_{SS} \approx \theta_{RR}$ and $\theta_{SR} \approx \theta_{RS}$), which was also observed. The reason for the approximate signs is because (a) there is a measurement error, and (b) two different films have to be created to do the measurement. This has an obvious and a subtle effect. The contact angle is a result of many chiral interactions across the surface (~1 mm dimension). The grafting procedure is imperfect: the density and detailed distribution of leucinol molecules on the wafer are in detail different each time. Also, the *SS* and *RR* (and *RS* and *SR*) interactions are not strictly enantiomeric because of the different arrangements of tethered molecules in each case. We expect the latter effect to be small.

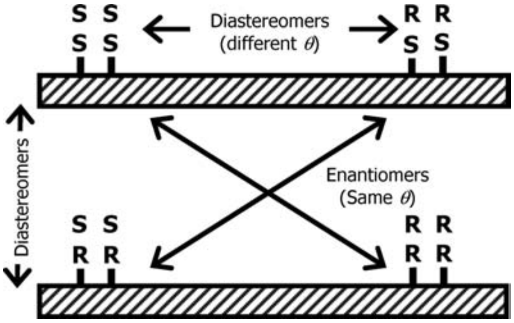


Figure 2. Different stereochemistries examined. For pairs labeled as enantiomers, the total interaction is not strictly enantiomeric because of the different distributions of grafted molecules.

Table 1. Contact Angles of Leucinol Droplets on a Leucinol-Modified Silicon Wafer in Hexadecane Medium[a]

hexadecane		LIQUID			
		S		R	
		θ_A	θ_R	θ_A	θ_R
SOLID	S	86 ± 3	56 ± 7	61 ± 12	20 ± 5
		86 ± 1	65 ± 4	75 ± 1	36 ± 5
	R	74 ± 1	61 ± 13	82 ± 1	56 ± 2

[a] Each reported value is the average ± variance of five measurements on a single wafer.

The results presented in Table 1 show that in fact the appropriate symmetry was observed for the advancing angles. The receding angles showed the same trend, but there was a large scatter in the results. The large hysteresis between the advancing and receding angles shows that the chiral films were imperfect. The reproducibility of the results was demonstrated by repeating the measurement with a separate *S* wafer, as shown by the two sets of results in Table 1 listed next to "SOLID *S*".

The contact angle can also be used to determine the interfacial tension, from which the energy of chiral discrimination can be calculated approximately. The Young equation gives the relationship between the interfacial tensions, γ, for the droplet. If we consider two different chiral liquids, L^R and L^S, on the same chiral solid, S^S, in the same achiral medium, M, then

$$\gamma_{S^SM} = \gamma_{S^SL^R} + \gamma_{L^RM}\cos\theta_{SR} \qquad (1)$$

$$\gamma_{S^SM} = \gamma_{S^SL^S} + \gamma_{L^SM}\cos\theta_{SS} \qquad (2)$$

Because the medium is achiral, the LM interaction is the same for the two enantiomers (i.e., $\gamma_{L^RM} = \gamma_{L^SM}$). Next, we assume that the solubility/vapor pressure of the chiral liquid in the medium is sufficiently low that the surface excess at the solid−medium interface is negligible, from which it follows that the left sides of eqs 1 and 2 are equal. Subtracting the two equations gives

$$\gamma_{S^SL^S} = \gamma_{S^SL^R} + \gamma_{L^SM}(\cos\theta_{SR} - \cos\theta_{SS}) \qquad (3)$$

Hence, the difference in the contact angles gives the difference in the solid−liquid interfacial tensions for the two enantiomeric liquid droplets. Now, to access the free energy of chiral discrimination per molecule for the chiral interaction, ΔG, we require the area per chiral molecule, a:

$$\Delta G = a\gamma_{L^SM}(\cos\theta_{SR} - \cos\theta_{SS}) \qquad (4)$$

We can use eq 4 to estimate the energy of chiral discrimination for leucinol in the film. This energy includes the lateral interactions between neighboring chiral molecules, which are usually far fewer in chromatography. First, we estimate that there is ~1 molecule/nm^2 in the film (i.e., $a \approx 1$ nm^2/molecule), and we arbitrarily use the advancing angle on the *S* film. We measured the interfacial tension to be $\gamma_{\text{leucinol-hexadecane}} = 3.6$ mN/m on the basis of the shape of a pendant drop. The result is $\Delta G = 1.1 \times 10^{-21}$J/molecule $\approx$ 0.007 eV $\approx 0.25k_BT$ at room temperature. This is in the range of previous measurements for chiral discrimination of (different) molecules[3,18] but was obtained here by a simple method.

The contact angle can be measured in a variety of immiscible media. We note that for a given chiral discrimination energy, the difference in cosines is inversely proportional to the liquid−medium surface tension, so bigger changes in cos θ are expected for smaller γ_{LM}. Of course, a medium should be chosen to ensure that θ is not zero, and because the cosine function is nonlinear, the changes in θ upon changing media also affect the resolution.

To test the effect of the medium, we also measured the contact angles in air, where γ_{LM} is 8 times greater than in hexadecane, expecting the difference in cos θ to be one-eighth that in hexadecane. The results, which are presented in Table 2, showed that the enantiospecificity of the contact angle was no longer resolved under this condition, as expected from eq 4.

Table 2. Contact Angles of Leucinol Droplets on a Leucinol-Modified Silicon Wafer in Air Medium

air		LIQUID			
		S		R	
		θ_A	θ_R	θ_A	θ_R
	S	43 ± 1	21 ± 1	35 ± 1	14 ± 2
SOLID	R	39 ± 2	20 ±4	39 ± 2	20 ± 8

Finally, we note that the energy of chiral discrimination can also be obtained from the difference in contact angle for the same enantiomer of the liquid on solids with a different enantiomer grafted to the surface. In this case, if we assume that the density of grafting is the same on the two solids, eq 4 becomes

$$\Delta G = a\gamma_{\mathrm{L}^{S}\mathrm{M}}(\cos\theta_{SR} - \cos\theta_{RR}) \qquad (5)$$

In conclusion, we have shown that chiral recognition can produce differences in the macroscopic contact angle. In addition, we have described a method for measuring the energy of chiral discrimination from two simple contact angle measurements.

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