

Chiral Discrimination Effects in Langmuir Monolayers of 1-*O*-Hexadecyl GlycerolN. Nandi<sup>†</sup>*Birla Institute of Technology and Science, Pilani, Rajasthan, 333031, India*D. Vollhardt<sup>\*,‡</sup> and G. Brezesinski<sup>§</sup>*Max-Planck-Institut für Kolloid- und Grenzflächenforschung, D-14424 Potsdam, Germany**Received: July 16, 2003; In Final Form: October 8, 2003*

Chiral discrimination effects in the monolayer of 1-*O*-hexadecyl glycerol (3-hexadecyl-oxy-propane-1,2-diol) amphiphile are theoretically investigated on the basis of a detailed coarse-grained molecular model. The theory uses experimentally obtained information for the average tilt and azimuthal orientation of a reference molecule and minimizes the energy of neighboring molecules using a theoretical framework developed previously. On the basis of the effective pair potential (EPP) of a neighboring pair of molecules, the mutual orientation at the minimum of EPP is obtained. The predicted curvature of the domains composed of enantiomeric amphiphiles based on the mutual orientation obtained from the EPP theory agrees with the experimentally observed handedness based on results from optical studies such as Brewster angle microscopy and fluorescence microscopy. The study revealed, for the first time, interesting crossover from heterochiral preference to homochiral preference of hexadecyl glycerol amphiphile. The theoretical result is consistent with the experimentally observed discrimination effects based on optical studies. The pair potential profiles of enantiomeric and racemic monolayers have similar features. However, the detailed distance and orientation dependences are different for enantiomeric and racemic pairs as revealed by the calculation of discrimination energy. Significant orientation dependence of chiral discrimination is observed which indicates that discrimination effects are not only dependent on intermolecular separation but also on their mutual orientation. The present study also indicates that the calculation of the magnitude of discrimination depends on the representation of molecular structure used in theoretical calculations and is consistent with our previous studies of different amphiphilic monolayers.

## Introduction

Chirality is observed from microscopic, mesoscopic, macroscopic biological and biomimetic systems.<sup>1,2</sup> This overwhelming presence of chirality is related with the origin of homochiral evolution.<sup>3</sup> In recent years, amphiphilic monolayers are used as model systems to understand the chiral discrimination by experiment as well as theory. The experimental techniques and related results are reviewed recently.<sup>1,2,4–7</sup> Molecular theories are proposed to understand the effect of the molecular chiral structure on the monolayer morphology.<sup>8–16</sup> Molecular theories seem most promising in explaining the experimental results on the mesoscopic domain morphology, as observed by optical techniques.<sup>11–16</sup> Different types of amphiphiles including amphiphiles with an amino acid headgroup, lipids, glycerol amine amphiphiles, etc., have been theoretically investigated.

Recently, domains with interesting shape and inner structure are observed in monolayers of 1-*O*-alkyl glycerol amphiphiles using isotherm studies, optical techniques (fluorescence microscopy and Brewster angle microscopy) as well as Grazing Incidence X-ray Diffraction technique.<sup>17–25</sup> These amphiphiles have a glycerolic headgroup in common. The isotherms as well

as the fluorescence images of enantiomeric and racemic 1-*O*-hexadecyl glycerol (3-hexadecyl-oxy-propane-1,2-diol; HOPD) are closely similar.<sup>17a</sup> The fluorescence microscopy studies at 20 °C reveal that the domains of racemate are initially with sharp edges and a defect at one side. They are pentagonal or hexagonal shaped with an indentation on the large side of the polygon. The notch becomes more pronounced with growth in the domain size. Gradually, with increase in pressure, branching starts and the branches themselves are also polygonal. Similar branching occurs in domains composed of only the *S*-enantiomer. However, in the later case, only clockwise branches are observed which reflects the effect on chirality. Overall, the features of enantiomeric and racemic amphiphiles are not drastically different. This similarity in the behavior of enantiomeric and racemic glycerol ether amphiphiles is unlike other amphiphiles such as lipids, amino acid amphiphiles, as well as alkylamine glycerols. In all the later cases, the domains of enantiomeric and racemic amphiphiles have clear distinctive features.<sup>1,2,11–16</sup> Fluorescence images of enantiomeric and racemic HOPD are shown in Figure 1.

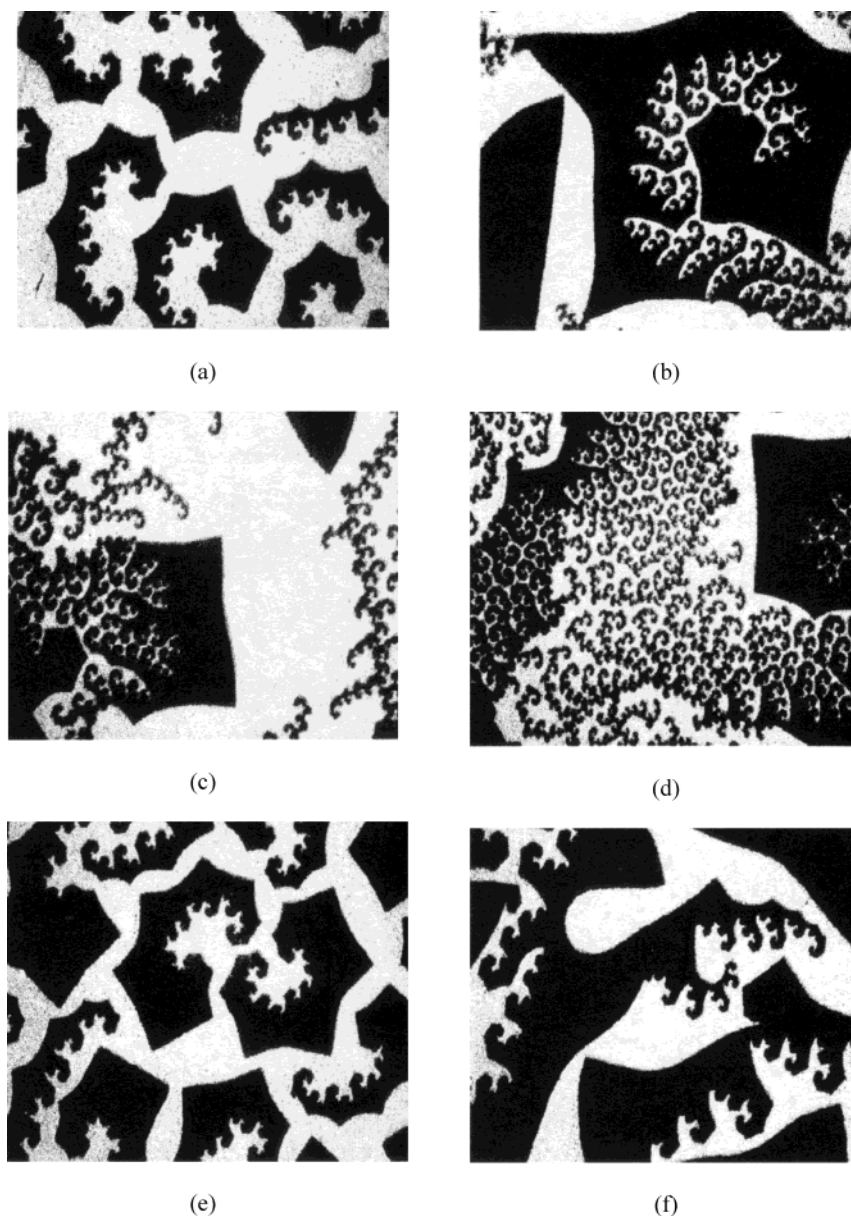
The Brewster angle microscopy (BAM) studies on racemic HOPD show interesting changes from polygonal shape at 35 °C to three-armed domain with segments at 15 °C.<sup>20</sup> Three to four armed domains are observed at temperatures as high as 23 °C. The arms of the domains have a defect line in the middle, and there are changes in the orientation within each segment.

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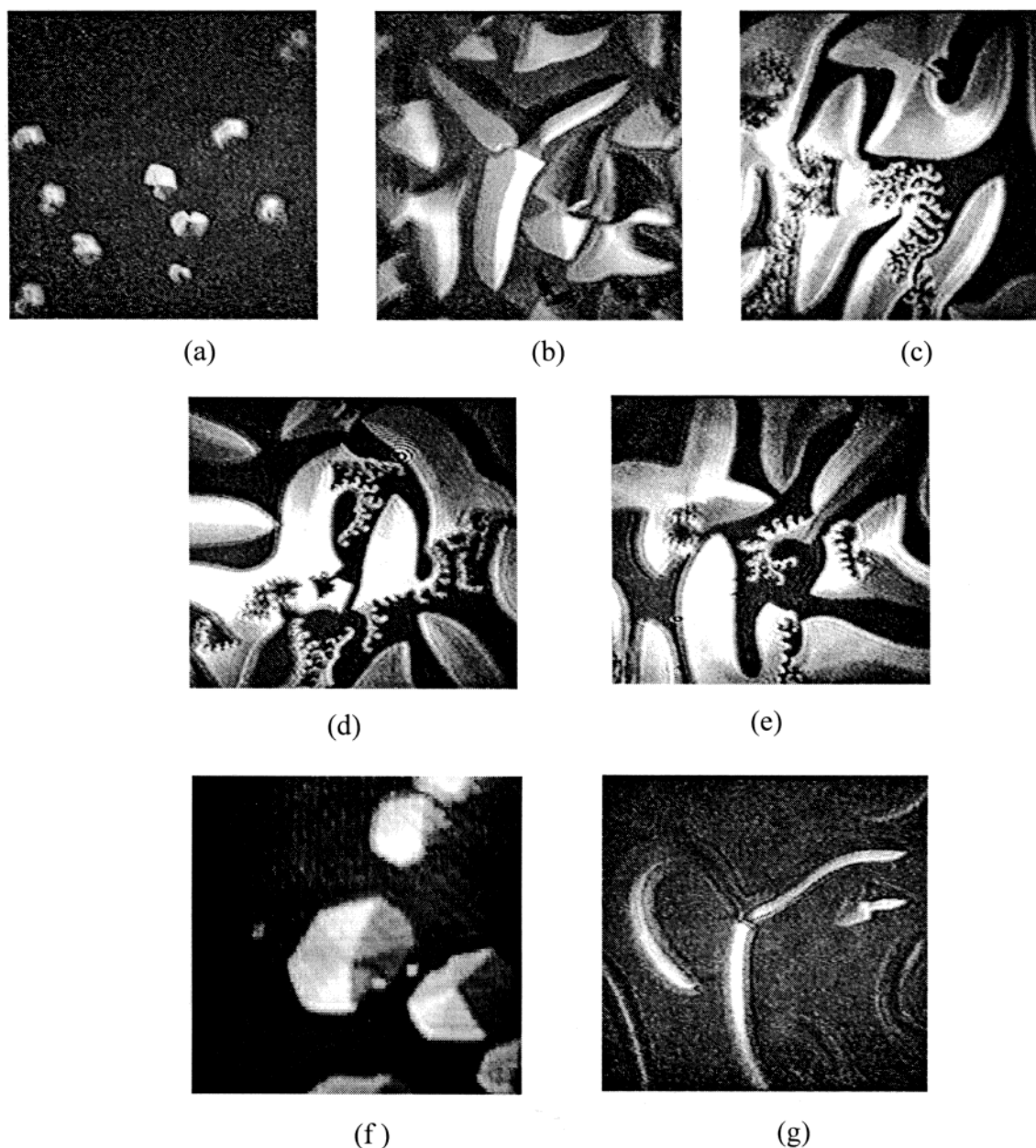


**Figure 1.** Fluorescence images of 1-*O*-hexadecyl glycerol monolayer domains. Figures (a) and (b) correspond to the *R*-enantiomer at 9.1 mN/m and 15.2 mN/m, respectively. Figures (c) and (d) correspond to the racemate at 11.9 mN/m and 18.1 mN/m, respectively. Figures (e) and (f) correspond to the *S*-enantiomer at 8.6 mN/m and 11.1 mN/m, respectively. All measurements are at 293.15 K.

BAM studies on enantiomeric HOPD shows similar features as observed by fluorescence microscopy. Detailed lattice structures are available using GIXD at low (at 5 °C) as well as higher temperature (at 20 °C).<sup>19</sup> The racemic lattice is centered rectangular for both temperatures over the whole pressure range investigated with a sharp transition of molecular tilt direction from *NN* to *NNN* from the low to high pressure phase at both temperatures. The enantiomeric lattice is oblique and the azimuth varies continuously from *NN* to *NNN* in contrast to the racemic lattice. BAM images of enantiomeric and racemic HOPD are shown in Figure 2. The BAM images show features similar to those observed with fluorescence microscopy. The variation in the domain shape in racemate is shown in Figure 2a–c, which shows the growth of spirals with increasing pressure. The direction of the curvature of the spirals in the racemic and *S*-enantiomeric domains is shown in Figure 2, parts d and e, respectively. The variation in the domain shape with temperature is shown in Figure 2f (measured at 308.15 K) and Figure 2g (measured at 288.15 K), respectively.

Phase behavior and domain shape of HOPD are complex.<sup>21</sup> The experimental results raise the question about the origin of apparent similarity in the behavior of enantiomeric and racemic monolayers. On the other hand, a signature of chiral discrimination is also observed in such systems.<sup>17a</sup> At 20 °C, the transition pressure of the *S*-enantiomer is above the value of the racemic mixture. This indicates a heterochiral preference over homochiral preference. The appearance of branches of opposite handedness from the same domain of racemates suggests a chiral segregation of the racemate into solid phases of two enantiomers. This indicates a homochiral preference above the transition pressure (observed from the break in the slope of the isotherm with a transition from the liquid expanded (LE) to liquid condensed (LC) phase. A molecular study of such a discrimination effect in HOPD monolayers is not yet carried out.

Recently, an effective pair potential (EPP) based theory is proposed to explain the domain shape of condensed phase monolayers.<sup>1,2,11–16</sup> The theory uses exact expressions for the orientation-dependent distance between the segments of a pair



**Figure 2.** BAM images 1-*O*-hexadecyl glycerol monolayer domains. Figures (a), (b), and (c) correspond to the racemate at molecular area 0.45 nm<sup>2</sup>/molecule, 0.35 nm<sup>2</sup>/molecule, and 0.3 nm<sup>2</sup>/molecule, respectively. In figures (d) and (e), the domains of racemate and *S*-enantiomers are shown, respectively, at 0.3 nm<sup>2</sup>/molecule. All measurements are at 296.15 K. The variation in domain shape is depicted in figures (f) and (g). Figure (f) is at 308.15 K, whereas Figure (g) is at 288.15 K.

of neighboring molecules.<sup>11,12</sup> Using these expressions in the form of a distant-dependent potential (Lennard Jones type), the effective pair potential is calculated as a function of the mutual orientation and the separation between a pair of molecules. The minimized energy configuration of the pair, as obtained from the EPP plot, gives the average mutual arrangement of a pair of neighboring molecules in the condensed phase, where the chiral structure-dependent interaction is significant. A number of mutual intermolecular arrangements are expected with variations of the intermolecular separation (with change in pressure) in an assembly of amphiphilic molecules. On an average, the minimum energy configuration would be most populated among the distribution of structures. This can be easily demonstrated by considering a distribution where the deeper minima will more significantly contribute to the total energy of aggregate compared to the relatively higher energy structures. It is assumed that the minimized energy pair configuration drives

the aggregate morphology in the condensed phase, where molecules are arranged in a next-to-next fashion. Thus, starting from the molecular structure and using the average molecular orientation (from experimental data such as GIXD), the EPP could predict the handedness of domains. The calculation is found to be insensitive to the choice of the parameters. However, the consideration of the explicit chiral structure in calculating the orientation-dependent distance between the pairs of molecules is found to be important. An atomistic or coarse-grained description of the molecular structure is better than the equivalent sphere description (where the groups attached to the chiral center are represented by the corresponding equivalent spheres) because the expression of the molecular chiral structure is reduced in the later representation. Recently a study on the orientation and distance-dependent chiral discrimination effect in amphiphilic monolayers is carried out on the basis of the EPP theory.<sup>15</sup> The study revealed an interesting distance and



orientation dependence of the chiral discrimination in amino acid and amide headgroup containing amphiphilic monolayers. It is worthwhile to carry out such a study with HOPD monolayers which exhibits interesting discrimination in the experimental results. In the present work we calculate the effect of chirality on the morphology of 1-*O*-hexadecyl glycerol (3-hexadecyl-oxy-propane-1,2-diol, HOPD) with the molecular formula  $C_{16}H_{33}-O-CH_2-CHOH-CH_2OH$  using the EPP-based theory. A coarse-grained molecular model is used to calculate the EPP of the HOPD molecule.

At first, some experimental details are given in section II. In the next section (section III) we present the brief details of the theoretical calculation. In section IV we present the results, which is followed by discussion. We present the concluding remarks in section V.

## II. Experimental Section

1-*O*-Hexadecyl-*rac*-glycerol (with a purity of  $\geq 99\%$ ) was obtained from Sigma. The enantiomeric *S*-form was a gift of C. Tschirske (Institute of Organic Chemistry, University of Halle, Germany) prepared with high enantiomeric purity according to ref 18. The amphiphiles were dissolved in a 9:1 (v:v) mixture of *n*-heptane (for spectroscopy, Merck) and ethanol (p.a., Merck) for spreading on the aqueous subphase. The subphase water used for the experiments was purified by a Millipore desktop unit (Millipore, Eschborn, Germany).

For the fluorescence microscopy studies, the Langmuir trough was integrated into a fluorescence microscope (Olympus, Japan) with a motor-driven *xy*-stage. The spread 1-*O*-hexadecylglycerol solution contained 0.5 mol-% 1-hexadecanoyl-2-(*N*-(7-nitrobenz-2-oxa-1,3-diazol-4-yl)amino)hexanoyl)-*sn*-glycero-3-phosphocholine (NBD-PC; Sigma, Munich) as fluorescence dye. Excitation of the fluorescence probe was achieved using a 100 W high-pressure mercury lamp. The monolayers were compressed continuously with an initial compression rate of 0.05 cm<sup>2</sup>/s up to the phase transition pressure, where the fluorescence microscopy measurements were performed. The NBD-PC fluorescence probe is preferentially partitioned into the disordered fluid phase.

A Brewster angle microscope (BAM 1+), NFT, Göttingen) mounted on a Langmuir trough was used for the BAM studies. The distortion of the digitized images were corrected with image-processing software. The lateral resolution of the BAM was approximately 4  $\mu$ m.

## III. Theoretical Formulation

In the present study, the tails and the heads of the molecule are represented by an array of collinear spherical groups (CH<sub>3</sub>, CH<sub>2</sub>, CH, O, etc.). Thus, whereas we neglect the atomistic details, the average orientations of the groups with respect to the chiral center are considered in detail over a reasonably small length scale. These tails and heads are denoted by the subscripts *t* and *h*, respectively. Such a coarse-grained description of the amphiphilic molecules is found to be useful in previous other studies.<sup>11–16</sup> The molecular segments are placed at the lattice positions. One molecule is chosen as reference and the other molecules are oriented as well as separated from it. The energy is calculated at each point of orientation and separation to sufficiently cover the energy profile. Note that the choice of the reference is completely arbitrary and the results of the calculation are independent of the choice. The orientation of the first molecule with respect to the normal ( $\mu$ ) as well as the angle between the azimuthal tilt direction of the tail (projected on the perpendicular plane to the normal) and the *X*-axis

**TABLE 1: Parameters for the Calculation of EPP of HOPD<sup>a</sup>**

| group           | $\sigma$ (Å) | $\epsilon/k_B$ (K) |
|-----------------|--------------|--------------------|
| CH <sub>3</sub> | 2.99         | 80.50              |
| CH <sub>2</sub> | 2.45         | 59.37              |
| CH              | 1.40         | 40.25              |
| O               | 2.96         | 105.66             |

<sup>a</sup> Temperature is 278.15 K in all cases.

(denoted by  $\alpha_i$ ) are obtained from the Grazing Incidence X-ray Diffraction (GIXD) data.<sup>17b</sup>

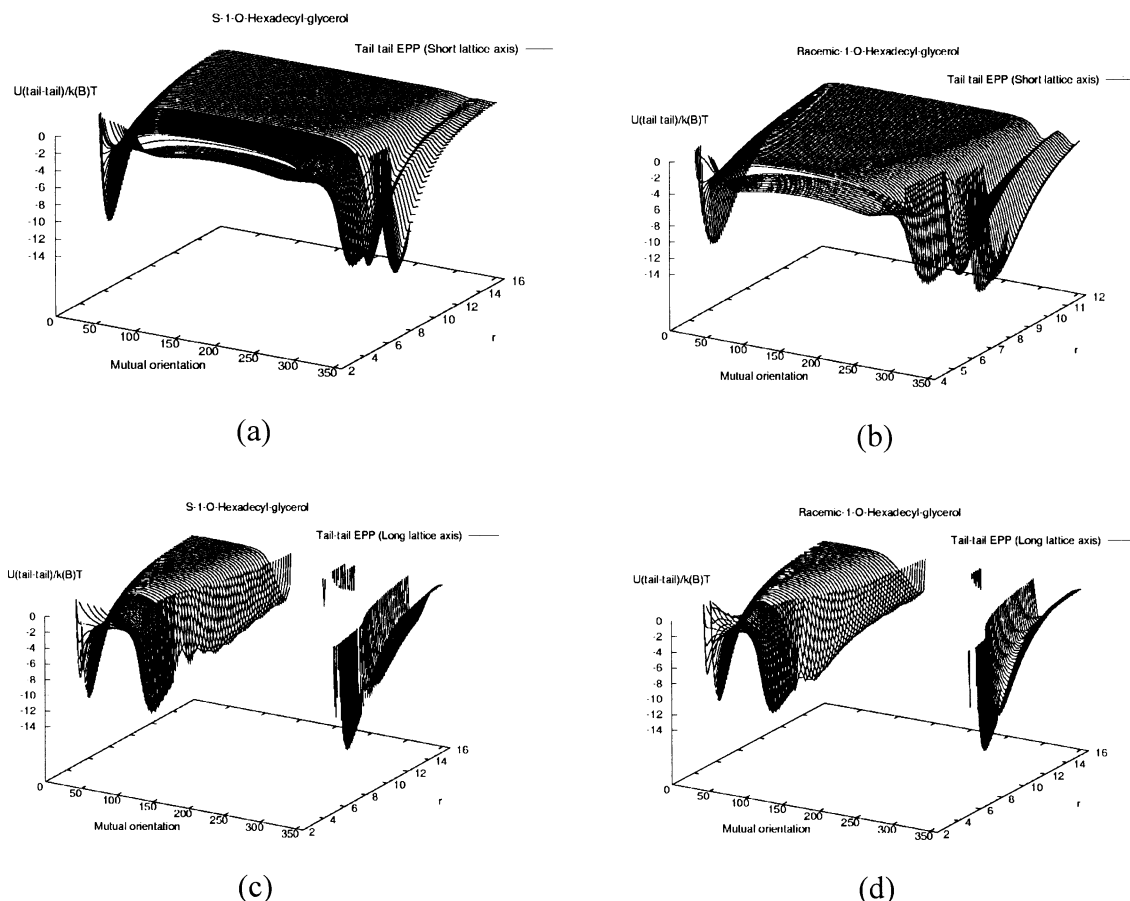
The effective pair potential between *i*th and *j*th molecules in the monolayer, each of which is composed of several groups (indicated by *g*(*i*) or *g*(*j*)), such as, CH<sub>3</sub>, CH<sub>2</sub>, CH, O, and OH, is calculated using a Lennard Jones pair potential, given by the form

$$U/k_B T = \sum_{g(i), g(j)} 4\epsilon/k_B T^{g(i)g(j)} [(s^{g(i)g(j)}/\sigma^{g(i)g(j)})^{-12} - (s^{g(i)g(j)}/\sigma^{g(i)g(j)})^{-6}]$$

Here,  $S^{g(i)g(j)}$  is the orientation-dependent separation between the interacting groups and exact expressions for such separations have been developed earlier.<sup>11,12</sup> The energy parameter is calculated by the Berthelot rule  $\epsilon^{g(i)g(j)} = \sqrt{\epsilon^{g(i)}\epsilon^{g(j)}}$  and the distance-dependent parameter  $\sigma^{g(i)g(j)}$  is given by the average of the diameters of the individual interacting groups  $(\sigma^{g(i)} + \sigma^{g(j)})/2$ . The related energy parameters and diameters are taken from the standard literature<sup>26</sup> and are shown in Table 1. The justification about the use of the coarse-grained approach to represent the molecular model is presented in earlier works.<sup>13–16</sup> It is also shown that the choice of a consistent set of parameters as well as the level of coarse graining of the molecular model leads to correct conclusions about the curvature or the discrimination.<sup>13–15</sup> A reference molecule is located according to the tilt and azimuthal projection experimentally observed. The neighboring molecule is rotated anticlockwise with respect to the reference molecule (denoted by  $\delta\alpha_i$  and varied by 360°) in the interfacial plane and simultaneously the distance between the pair of molecules is gradually changed. The pair potential is calculated at each position of the mutually oriented state of the pair of molecules. The tilt of the headgroups in the aqueous subphase is unknown. Thus, the EPP of the headgroup is calculated as a function of three variables: first, the separation of neighboring headgroups; second, the orientation of the headgroup from the normal to the interface in the air to water (*-Z*) direction (denoted by  $\beta_h$  and varied by 180°); and third, the mutual orientation of neighboring headgroups (denoted by  $\delta\alpha_h$  and varied by 360°). The  $\beta_h$  value corresponding to the energy minima is used to obtain the EPP of the headgroup as a function of the mutual separation and  $\delta\alpha_h$ .

## IV. Results and Discussion

The EPP of the pair of neighboring tails of the enantiomeric (*S*-) and racemic 1-*O*-hexadecyl glycerol molecules along the short lattice axis are presented in Figure 3a and Figure 3b, respectively. The EPP of the *S*-enantiomeric pair as shown in Figure 3a is closely similar to that of the racemic pair shown in Figure 3b. The EPP of both enantiomeric and racemic pair have deep minima at certain orientations and the EPP is unfavorable at the intermediate range of orientations. The minimum value of EPP is  $-13.81 k_B T$  at  $\delta\alpha_i = 359^\circ$  for the *S*-enantiomeric pair. Similar features are observed in the EPP of the pair of neighboring tails of enantiomeric (*S*-) and racemic



**Figure 3.** The EPP of the pair of neighboring tails of enantiomeric (*S*-) and racemic 1-*O*-hexadecyl glycerol molecules along (a) the short lattice axis of *S*-enantiomeric pair, (b) short lattice axis of racemic pair (c) long lattice axis of *S*-enantiomeric pair (d) long lattice axis of racemic pair. All results are at 278.15 K.

molecules along the long lattice axis. The EPP plots are shown in Figure 3c and Figure 3d, respectively. The minimum value of EPP is  $-13.64 k_B T$  at  $\delta\alpha_t = 350^\circ$  for the *S*-enantiomeric pair along the long lattice axis.

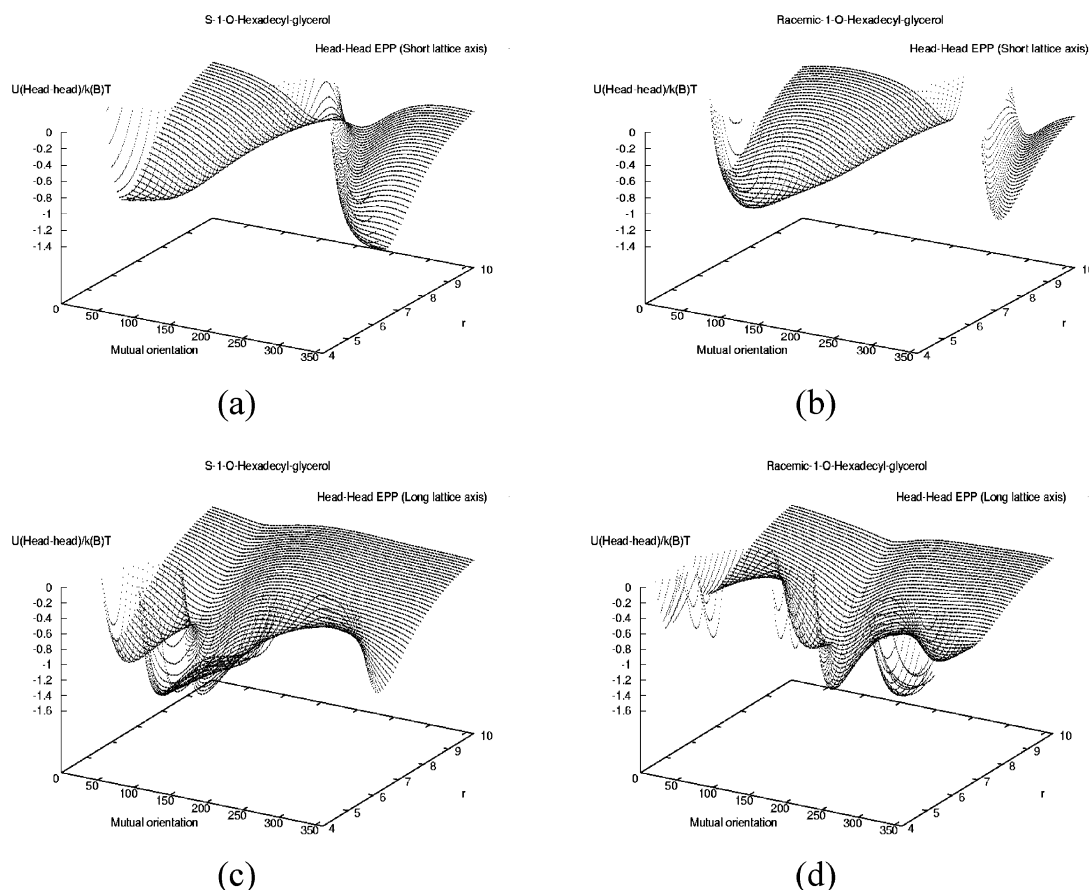
The calculated orientation at the EPP minimum of the *S*-enantiomeric pair indicates that with respect to a reference molecule placed at a corner of the lattice (closest to the observer), all other molecules orient in the  $\delta\alpha_t$  range between  $350^\circ$  and  $359^\circ$  (orientation considered in an anticlockwise way with respect to the projection of the reference molecule). Thus, the cooperative nature of orientation of the molecules is clockwise for the *S*-enantiomer. This theoretical conclusion is consistent with the experimental orientation of arms developed from the *S*-enantiomeric domain.

The minimum value of EPP is  $-13.80 k_B T$  at  $358^\circ$  for the racemic pair (*S*- and *R*-). The minimum EPP value is  $-13.58 k_B T$  at  $347^\circ$  for the racemic pair (*S*- and *R*-). By mirror-image relationship, the mutual orientation of *R*- and *S*-pairs should be opposite to that of the respective *S*- or *R*-pair. Thus, an opposite handedness is expected in the later case.

The EPP of the pair of the neighboring headgroups of the enantiomeric (*S*-) and racemic 1-*O*-hexadecyl glycerol molecules along the short lattice axis are presented in Figure 4a and Figure 4b, respectively. Similar to the tail part, the EPP of the *S*-enantiomeric pair (Figure 4a) is closely similar to that of the racemic pair (Figure 4b). However, due to the relatively lower number of groups present in the headgroup (compared to the tail segment) the magnitude of the minima of the headgroup pairs is less deep than the corresponding EPP of tails. The EPP of both the enantiomeric and racemic pair is relatively shallow

(compared to the corresponding tail) minima at certain orientations and the EPP is unfavorable at the intermediate range of orientations. The minimum EPP value is  $-1.26 k_B T$  at  $\delta\alpha_h = 359^\circ$  and  $\beta_h = 336^\circ$  for the *S*-enantiomeric pair and it is  $-1.22 k_B T$  at  $\delta\alpha_h = 59^\circ$  and  $\beta_h = 329^\circ$  for the racemic pair (*S*- and *R*-) along the short axis. The EPP plots of the headgroups along the long lattice axis are shown in Figure 4c and Figure 4d, respectively. The minimum EPP value is  $-1.44 k_B T$  at  $\delta\alpha_h = 136^\circ$  and  $\beta_h = 336^\circ$  for *S*-enantiomeric pair and it is  $-1.47 k_B T$  at  $\delta\alpha_h = 179^\circ$  and  $\beta_h = 329^\circ$  for the racemic pair (*S*- and *R*-). In all cases the energy of the headgroup pair is close to  $\sim k_B T$ . Thus, we expect that the thermal energy will lead to a distribution of headgroup orientations in the aqueous subphase.

Despite the apparent similarity in the overall EPP profiles of tails and headgroups of enantiomeric and racemic molecules, the distance and orientation dependence are different in the two cases. The difference between EPP of the racemic and enantiomeric pairs  $[U(\text{Racemic}) - U(\text{Enantiomeric})]/k_B T$  of tails along the short axis are plotted in Figure 5a–c. Only negative EPP values are considered in calculating the difference (denoted by  $\Delta U_{\text{dis}}$ ). Only favorable free energies are expected to contribute to the stable monolayer morphology. Hence, a comparison of negative EPP values at each mutual separation and distance is relevant. The quantity  $\Delta U_{\text{dis}}$ , thus, denotes how the racemic pair is more stable over the enantiomeric pair. If this quantity is negative, then it corresponds to heterochiral preference and if it is positive, it indicates homochiral preference in the later case. We plotted the complete range of  $\Delta U_{\text{dis}}$  of tail–tail EPP along the short axis in Figure 5a and its negative and positive ranges in Figures 5b and 5c, respectively. It is



**Figure 4.** The EPP of the pair of neighboring headgroups of enantiomeric (*S*-) and racemic 1-*O*-hexadecyl glycerol molecules along (a) short lattice axis of *S*-enantiomeric pair, (b) short lattice axis of racemic pair, (c) long lattice axis of *S*-enantiomeric pair, (d) long lattice axis of racemic pair. All results are at 278.15 K.

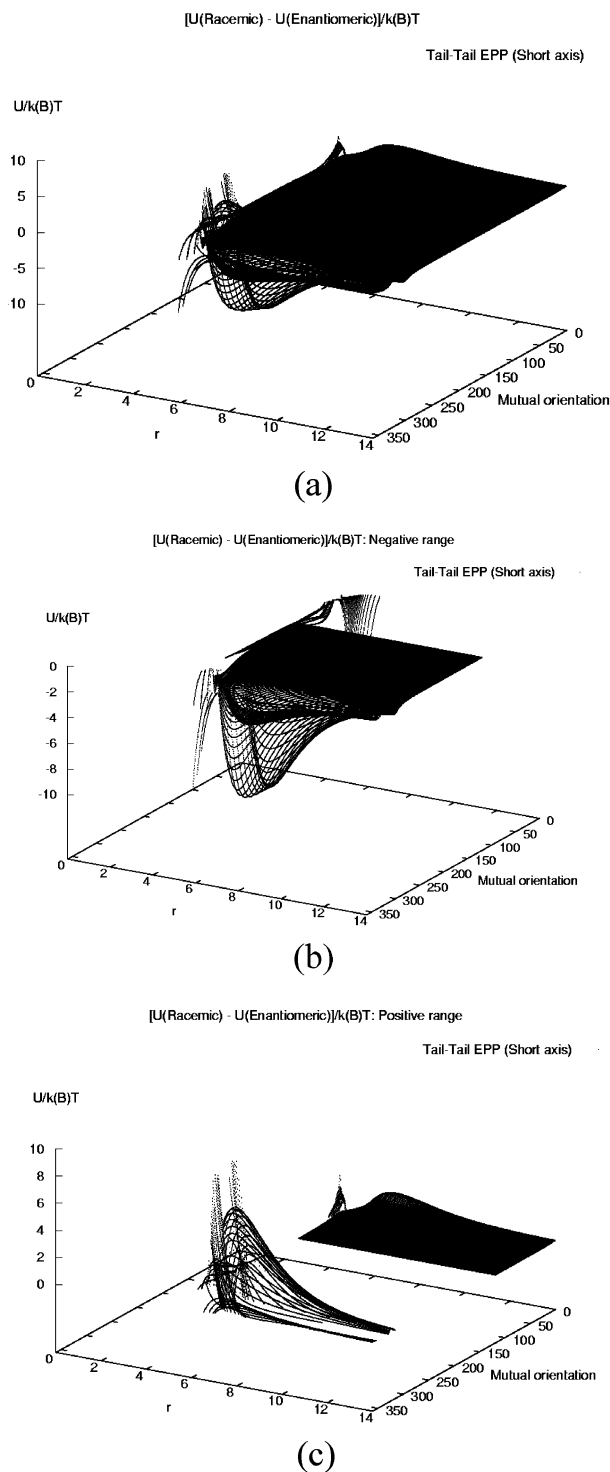
clearly seen that whereas  $\Delta U_{\text{dis}}$  is negative (indicating a heterochiral preference) for intermediate mutual separation (Figure 5b), gradually  $\Delta U_{\text{dis}}$  is positive (indicating a homochiral preference) for relatively shorter separations (Figure 5c). At very short separation, strong repulsion develops between the molecules and such configurations are strongly unfavorable. It is well-known that chirality-dependent interactions are not dominant at relatively larger separations (corresponding to the expanded phase) and the  $\Delta U_{\text{dis}}$  approaches zero in this case. However,  $\Delta U_{\text{dis}}$  is also strongly orientation dependent, as seen in Figure 5a–c.

Similarly, the difference between EPP of the racemic and enantiomeric pairs ( $\Delta U_{\text{dis}}$ ) of tails along the long axis are plotted in Figures 6(a–c), the difference between EPP of racemic and enantiomeric pairs ( $\Delta U_{\text{dis}}$ ) of the headgroups along the short axis are plotted in Figure 7a–c and the difference between EPP of the racemic and enantiomeric pairs ( $\Delta U_{\text{dis}}$ ) of the headgroups along the long axis are plotted in Figure 8a–c). The general features are same in all sets of plots i.e.,  $\Delta U_{\text{dis}}$  is negative (a heterochiral preference) for intermediate mutual separation (part b in Figures 5–8) and gradually  $\Delta U_{\text{dis}}$  is positive (a transition to homochiral preference) for relatively shorter separations (part c in Figures 5–8).

The transition from heterochiral preference to homochiral preference theoretically observed with the decrease in the intermolecular separation (corresponding to compression of the monolayer) predicts that the monolayer phase may prefer a chiral segregation with gradual compression. This theoretical prediction is in agreement with the experimental observation based on a comparison of surface pressure isotherms and fluorescence

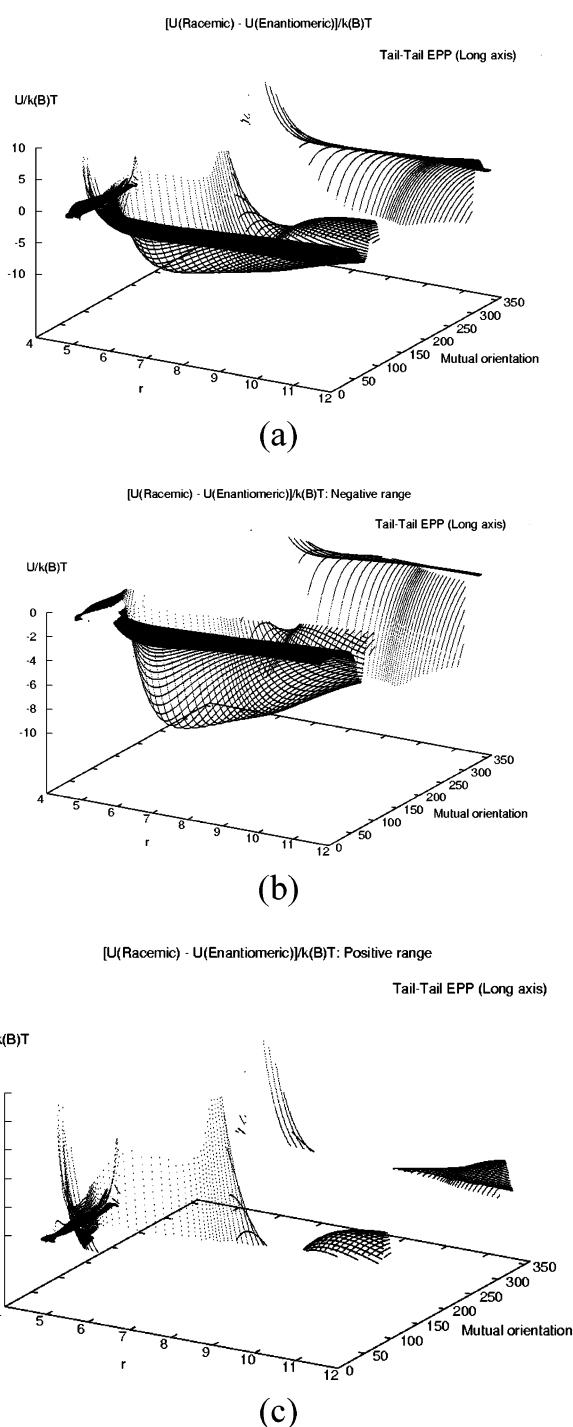
microscopy studies.<sup>17a</sup> As mentioned previously, at 20 °C, the transition pressure of the *S*-enantiomer is above the value of the racemic mixture, which indicates a heterochiral preference. The appearance of branches of opposite handedness from the same domain of racemates indicates chiral segregation of the racemic monolayer into solid phases of the two enantiomers. This suggests homochiral preference above the transition pressure.

In our preceding work,<sup>15</sup> distance- and orientation-dependent homochiral and heterochiral interaction is observed in a Langmuir monolayer of palmitoyl aspartic acid, stearoyl serine methyl ester, and tetradecyl dihydroxy pentanoic acid amide on the basis of an equivalent sphere model of amphiphiles. An important theoretical observation was that homochirality is preferred at shorter separation whereas heterochiral interaction is at larger separation. The distance dependence of the crossover from heterochirality to homochirality is consistent with the other theoretical calculation<sup>9,10</sup> based on the tripodal model of Andelman and de Gennes.<sup>8</sup> A novel observation of the EPP-based model<sup>15</sup> was the orientation dependence of the crossover from heterochirality to homochirality. The discrimination has significant orientation dependence and all orientations are not equally favored for homo- or hetero- chiral preference. However, due to the use of the equivalent sphere-based model, the magnitude of the discrimination is a few  $k_B T$  for the palmitoyl aspartic acid, stearoyl serine methyl ester, and tetradecyl dihydroxy pentanoic acid amide amphiphiles. It is known that due to the reduction of the molecular chiral features in the equivalent sphere representation (by considering the groups as equivalent spheres), the EPP magnitudes are also reduced (for



**Figure 5.** The difference of EPP of tails of racemic pairs and enantiomeric (*S*-) pairs of 1-*O*-hexadecyl glycerol molecules ( $U(\text{Racemic pair})/k_B T - U(\text{Enantiomeric pair})/k_B T = \Delta U_{\text{dis}}$ ) along short lattice axis calculated from favorable pair potentials in Figure 3. (See text for details.) For (a) complete range of calculated  $\Delta U_{\text{dis}}$ , (b) only negative range of calculated  $\Delta U_{\text{dis}}$ , (c) only for positive range of calculated  $\Delta U_{\text{dis}}$ . All results are at 278.15 K.

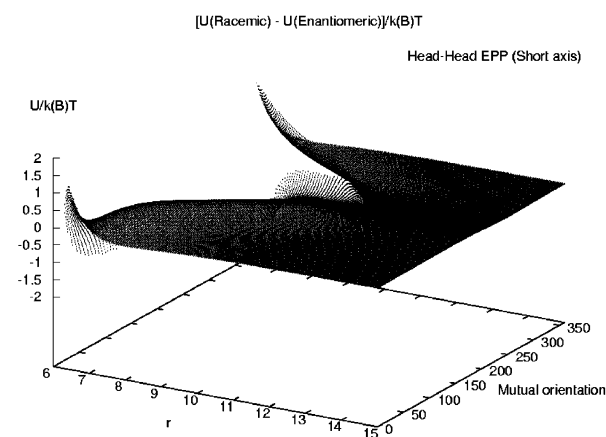
a comparison of the coarse-grained and equivalent sphere representation, we refer to the preceding work<sup>15</sup>). The present calculation of the discrimination energy in 1-*O*-hexadecyl glycerol system using coarse-grained description confirms this conclusion. In the later work one can observe greater magnitudes of  $\Delta U_{\text{dis}}$  of tails for both of its homochiral and heterochiral part.



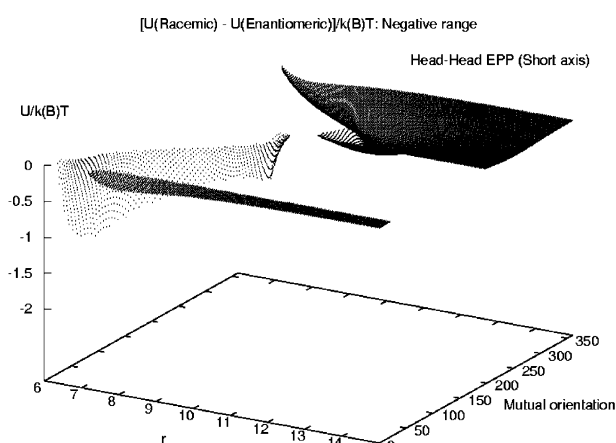
**Figure 6.** The difference of EPP of tails of racemic pairs and enantiomeric (*S*-) pairs of 1-*O*-hexadecyl glycerol molecules ( $U(\text{Racemic pair})/k_B T - U(\text{Enantiomeric pair})/k_B T = \Delta U_{\text{dis}}$ ) along long lattice axis calculated from favorable pair potentials in Figure 3. (See text for details.) For (a) complete range of calculated  $\Delta U_{\text{dis}}$ , (b) only negative range of calculated  $\Delta U_{\text{dis}}$ , (c) only for positive range of calculated  $\Delta U_{\text{dis}}$ . All results are at 278.15 K.

Thus, combined theoretical and experimental (fluorescence and Brewster angle microscopy) study of hexadecyl glycerol system provides understanding about interesting chiral discrimination at air/water interface. Due to the complex nature of phase transition in such systems (as indicated in the Introduction) more molecular studies are required in this direction. The effect of orientation-dependent ordering is worth investigating on the basis of the present approach. It may be noted that the

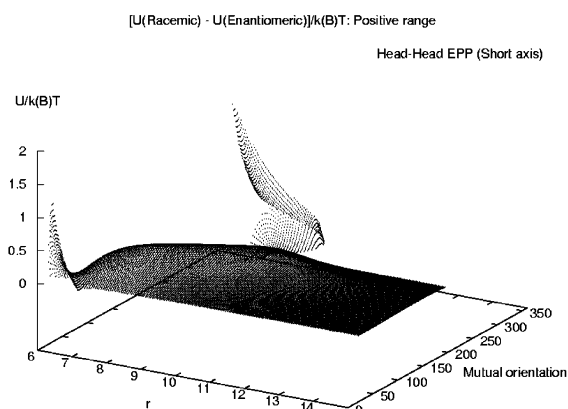




(a)



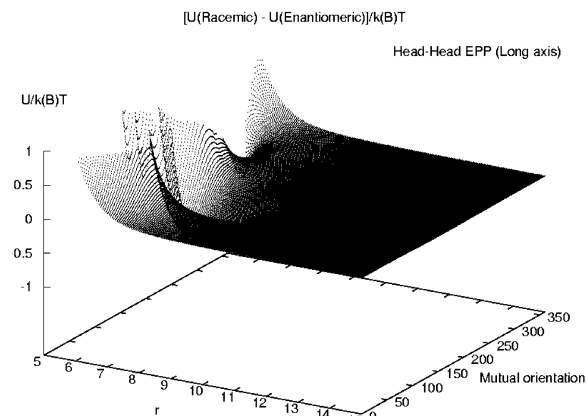
(b)



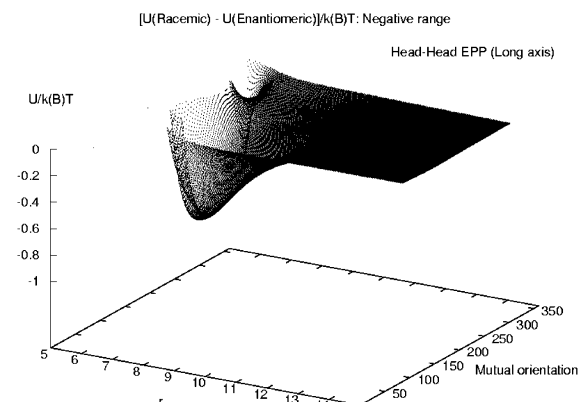
(c)

**Figure 7.** The difference of EPP of headgroups of racemic pairs and enantiomeric (*S*-) pairs of 1-*O*-hexadecyl glycerol molecules ( $U(\text{Racemic pair})/k_B T - U(\text{Enantiomeric pair})/k_B T = \Delta U_{\text{dis}}$ ) along short lattice axis calculated from favorable pair potentials in Figure 4. (See text for details.) For (a) complete range of calculated  $\Delta U_{\text{dis}}$ , (b) only negative range of calculated  $\Delta U_{\text{dis}}$ , (c) only for positive range of calculated  $\Delta U_{\text{dis}}$ . All results are at 278.15 K.

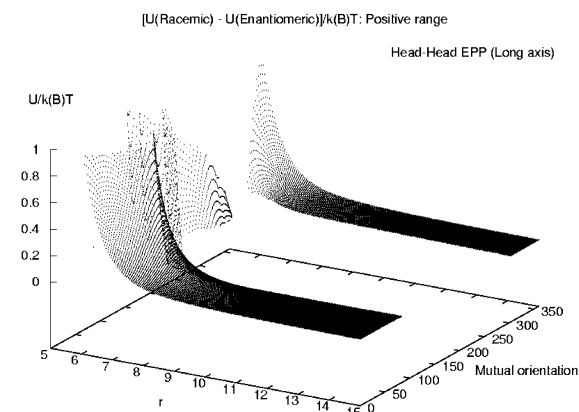
discrimination free energy is related to the discrimination internal energy and discrimination entropy by the standard thermodynamic relation, as studied by Andelman and Orland.<sup>9</sup> The distance dependence of these quantities is discussed. The relative contribution of the discrimination internal energy and the ordering effect (entropic) is currently under investigation.



(a)



(b)



(c)

**Figure 8.** The difference of EPP of heads of racemic pairs and enantiomeric (*S*-) pairs of 1-*O*-hexadecyl glycerol molecules ( $U(\text{Racemic pair})/k_B T - U(\text{Enantiomeric pair})/k_B T = \Delta U_{\text{dis}}$ ) along long lattice axis calculated from favorable pair potentials in Figure 4. (See text for details.) For (a) complete range of calculated  $\Delta U_{\text{dis}}$ , (b) only negative range of calculated  $\Delta U_{\text{dis}}$ , (c) only for positive range of calculated  $\Delta U_{\text{dis}}$ . All results are at 278.15 K.

The orientation dependence of these quantities could be of particular interest.

## V. Conclusions

The study revealed, for the first time, interesting crossover from heterochiral preference to homochiral preference of the



1-*O*-hexadecyl glycerol amphiphile in Langmuir monolayers. The chiral molecular structure and the lattice packing found play an important role in driving the preferred molecular orientation in the condensed phase. The theoretical result is consistent with the discrimination effects experimentally observed. The pair potential profiles of the enantiomeric and racemic monolayers have similar features. However, the distance and orientation dependences are different for enantiomeric and racemic pairs, as revealed by the calculation of discrimination energy. An interesting orientation dependence of the chiral discrimination is observed which indicates that both homo- and heterochiral discriminations are not only dependent on the interpair separation but also on their mutual orientation. Whereas the intermolecular distance dependence of chiral discrimination is also observed in other theoretical models, the orientation dependence of chiral discrimination is a new observation from the EPP theory. The present study also indicates that the calculation of the magnitude of discrimination depends on the representation of the molecular structure used in the theoretical calculation and is consistent with our previous calculations. The predicted curvature of domains composed of enantiomeric amphiphiles agrees with the experimentally observed handedness obtained from Brewster angle microscopy and fluorescence microscopy studies.

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