Theory of phase separation of binary self-assembled films

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Abstract

The thermodynamic properties of self-assembled monolayer (SAM) films composed of long and short alkanethiol chains are predicted from the statistical mechanical calculation and the dynamic Monte Carlo simulation, analogous to the Ising spin model in conjunction with interaction energy between the long and the short chains. Numbers of pairs of long–short chains are obtained for the interaction energy of the long–short chain and molar fractions. These relations are compared with the experimental result of binary SAMs, in which a small voltammetric wave appeared at a potential between two potentials of the desorbed reduction waves of long and short chains (J. Electroanal. Chem. 444 (1998) 113). The small wave can be ascribed to a new redox state generated by the interaction between the short and the long chains. The comparison estimates the interaction energy between the closest neighboring methylene groups to be 7.4 kJ mol$^{-1}$ at 25 °C. A pair of long–short chains is more unstable than pairs of long–long and short–short chains, and hence the long and short chains produce their own macroscopic phases. Monte Carlo simulation supports the appearance of the phase domains. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Alkane chains containing sulfur adsorb irreversibly onto a gold surface to form stable monolayers [1], called self-assembled monolayer (SAM) films. These films can exhibit a variety of functionalities by the introduction of chemical substituents at the end of alkane chains [2–31]. The SAM can also be modified with spontaneous coadsorption of two thiols from a binary mixed solution to yield a composite SAM [32]. This technique is useful for creating a continuous variation of functionalities by varying the molar fractions of the adsorbates. Basic studies on binary component systems have been directed toward electron transfer [11,14,33], wetting [1,27,34–43], and electrochemical charge [29]. A binary composite SAM generally occurs either as a microscopically mixed phase or as two separate phases. Some binary SAMs [34–36,44,45] have shown homogeneous phases that have no detectable domains. In contrast, some authors [42,46–50] have suggested the presence of phase separation on a nanometer scale. The homogeneous mixture seems to be associated with a good affinity between two kinds of adsorbates. The affinity may generate a new redox state [44], which gives a new voltammetric wave at a potential between two potentials of the two reductive desorption waves [42]. As an example, Fig. 1 shows cyclic voltammograms of binary SAMs composed of 3-mercaptopropionic acid (MPA) and 1-hexadecanethiol (HDT), obtained by Hobara et al. [42]. The cathodic waves are due to desorption of MPA and HDT at $-0.65$ and $-1.08$ V, respectively. The increase in the molar fraction, $X$, of MPA obviously increases the ratio, $\theta$, of the reduction charge of MPA, as is shown in Fig. 2. However, the sum of the charges for MPA and HDT at $-0.65$ and $-1.08$ V, respectively. The increase in the molar fraction, $X$, of MPA obviously increases the ratio, $\theta$, of the reduction charge of MPA, as is shown in Fig. 2. However, the sum of the charges for MPA and HDT is not conserved, suggesting the presence of a new intermediate species (Fig. 2). The intermediate is akin to the mixed-valence state of a multi-nuclear complex from the viewpoint of interaction [51,52].

It has been well recognized that phase separation is caused on a molecular scale by the interaction energy between neighboring molecules, as is known from the van der Waals equation [53]. When the interaction energy between hetero-species is predominant to that between homo-species, a phase separation is likely to
Fig. 1. Cyclic voltammograms of binary SAMs of MPA and HDT at the ratio of $X = 0.900$ (solid) and $X = 0.950$ (dotted line), taken from Ref. [42, Fig. 1].

Fig. 2. Dependence of normalized charge of reduction waves in the self-assembled thiol monolayers composed of 1-hexadecanethiol (HDT) and 3-mercaptopropionic acid (MPA) on the molar fraction ($X$) of MPA in the solution, cited from Ref. [42, Fig. 3]. The charge has been attributed to (○) MPA, (●) HDT and (♦) interactive species.

occur. A quantitative approach of phase separation has been described by the two- or three-dimensional Ising model of spins at which phases are formed at a temperature lower than a critical temperature [54]. Some modifications of the Ising model have been applied to electrochemical systems such as adsorption/desorption [55], LB films [56], multi-nuclear complexes with mixed-valence states [52,57], conducting polymers [58], and pH-variations on SAMs [59]. Although these successfully described a relation between the molecular interaction energy and some thermodynamic quantities, they did not mention size or distributions of domains that could be observed in terms of STM.

This paper aims at obtaining a quantitative relation between the interaction energy and the formation of domains for binary SAMs. The relation may be derived from a modification of the Ising model. The present report consists of two parts: 1. the derivation of the analytical expression for the number of pairs of the long and short chains in a one-dimensional model in order to formulate a relationship between the number of pairs and the pair interaction energy, and 2. the dynamic Monte Carlo simulation on a (111) crystal surface in order to access the possibility of forming phases composed of long or short chains. Analytical solutions predict only thermodynamically averaged quantities, but do not answer which patterns are formed. In contrast, the Monte Carlo simulation provides not only the thermodynamic quantities but also distributions as well as domain sizes.

2. Theory for one-dimensional arrangement

The SAM is assumed to be composed of a long chain, A, and a short chain, B, which are adsorbed compactly on a crystal surface without defects. The surface conventionally used is a (111) crystal face, on which adsorbates are arranged in a two-dimensional hexagonal configuration. Unfortunately, the two-dimensional configuration makes counting the numbers of pairs $A-A$, $A-B$ and $B-B$ quite difficult. We simplify it to a one-dimensional configuration, i.e. a linear combination of A and B. The linear combination is further simplified to that of a ring in order to avoid edge effects.

At first, we consider rings composed of three chains, as is shown in Fig. 3, and then extend this concept to a very large number of chains. We let pair interaction energies for $A-A$, $B-B$ and $A-B$ be $u_{AA}$, $u_{BB}$ and $u_{AB}$, respectively. Then, the Hamiltonian at each configuration contains interaction energies as well as the chemical potential of A ($\mu_A$) or B ($\mu_B$). If pair interaction energies are additive [52,57], the Hamiltonians corresponding to the configurations in Fig. 3 are expressed by

$$H_1 = 3\mu_A + 3u_{AA}$$
$$H_2 = 2\mu_A + \mu_B + u_{AA} + 2u_{AB}$$
$$H_3 = \mu_A + 2\mu_B + 2u_{AB} + u_{BB}$$
$$H_4 = 3\mu_B + 3u_{BB}$$

The partition function of all the configurations is given by

Fig. 3. Four-ring configurations composed of three species.
where \( \beta = 1/k_B T \) (\( k_B \): Boltzmann’s constant), and the pre-exponential factor, 3, implies three rotational isomers with identical energies.

The configuration in Fig. 3(a) has three pairs of AA, whereas the configuration of Fig. 3(b) has three rotational isomers, each including a pair of AA. Therefore, the expected value of taking the pair AA is given by

\[
\theta_{AA} = \left[ 3 \exp(-\beta H_1) + 3 \exp(-\beta H_2) + 3 \exp(-\beta H_3) \right] / Z
\]

In contrast, two pairs of AB are included in the three isomers of Fig. 3(b) and (c). Thus, the expected value of taking the pair AB is expressed by

\[
\theta_{AB} = \left[ 6 \exp(-\beta H_2) + 6 \exp(-\beta H_3) \right] / Z
\]

The composition of the SAM varies with the solution composition, because the SAM is in equilibrium with A and B. In other words, species A in the SAM can be regarded to be in equilibrium with B in the SAM through the equilibrium in the solution [35]. The reaction model is illustrated in Fig. 4. A measure of the equilibrium is the difference in the chemical potentials of A and B, \( \Delta G = \mu_A - \mu_B \), which is equivalent to the apparent electrode potential:

\[
E = \Delta G / e = (\mu_A - \mu_B) / e
\]

if A and B are electroactive species. According to the theory of the cooperative phenomenon for the multinoval metal complexes [52], the difference between \( u_{AA} \) and \( u_{BB} \) is compensated with the potential \( E \). Thus, a value of \( u_{AA} \) can be regarded as a value of \( u_{BB} \) without a loss of generality. Dividing Eqs. (6) and (7) by \( \exp(-\beta H_4) \) and using the following variable:

\[
u = u_{AA} - u_{AB}
\]

we can reduce Eqs. (6) and (7) to

\[
\begin{align*}
\theta_{AA} &= 3 \left( e^{-3\zeta} + e^{-2\zeta + 2\mu} \right) \\
\theta_{AB} &= 6 \left( e^{-3\zeta} + e^{-2\zeta + 2\mu} + 3e^{-\zeta + 2\mu} + 1 \right)
\end{align*}
\]

Fig. 4. Reaction model of the binary SAM. Species A and B in solution (sltn) are in equilibrium with \( A_{SAM} \) and \( B_{SAM} \) in the monolayer, respectively. Electrode reductions of \( A_{SAM} \) and \( B_{SAM} \) cause the desorption of each SAM at potentials \( E_A \) and \( E_B \), respectively. The difference between \( E_A \) and \( E_B \) gives an apparent equilibrium potential, \( E \), as defined in Eq. (8).

\[
Z = \exp(-\beta H_1) + 3 \exp(-\beta H_2) + 3 \exp(-\beta H_3) + \exp(-\beta H_4)
\]

where \( \zeta = FE/RT \). Obviously we have \( \theta_{BB} = 1 - \theta_{AA} - \theta_{AB} \). The variation of \( \theta_{BB} \) with \( \zeta \) at a given value of \( \beta \mu \) is a sigmoid (not shown here), similar to a steady-state voltamgram at a microelectrode. In contrast, the variation of \( \theta_{AB} \) with \( \zeta \) has a peaked shape. These variations are as expected. However, they are not useful for quantitative analysis of the experimental data (Fig. 2) because the three-chain model is too simple to reproduce the behavior of a real SAM. The number of chains should be increased to the order of \( 10^3 \).

In order to derive \( Z \) for extremely large \( N \), we apply the technique of statistical mechanics for the charge interaction of N-conjugated metal complexes [57] to this system. The Hamiltonian for the interaction of N adsorbates is given by [57]

\[
H(N) = \frac{N}{2} (\mu_A + \mu_B + u_{AA} + u_{AB})
\]

\[
+ \frac{\mu_A - \mu_B}{2} \sum_{i=1}^{N} s_i + \frac{u_{AA} - u_{AB}}{2} \sum_{i=1}^{N} s_is_{i+1}
\]

\[
\quad \text{where } s_i \text{ denote } 1 \text{ for } A \text{ or } -1 \text{ for } B, \text{ and } s_{N+1} = s_1.
\]

For example, the configuration in Fig. 3(b) corresponds to \( N = 3, s_1 = 1, \) and \( s_2 = s_3 = -1 \), which yield Eq. (2).

The partition function for \( H(N) \) is represented by

\[
Z = \sum_{s_1 = -1}^{1} \sum_{s_2 = -1}^{1} \cdots \sum_{s_N = -1}^{1} \exp(-\beta H(N))
\]

The analytical expression for this summation can be derived with the help of the auxiliary function [54]:

\[
g(s_is_{i+1}) = \exp[-\zeta(s_i + s_{i+1})/4 - (\beta \mu/2)s_is_{i+1}]
\]

Then \( Z \) is rewritten as

\[
Z = \exp\left[ -\frac{\beta N}{2} (\mu_A + \mu_B + u_{AA} + u_{AB}) \right]
\]

\[
\times \sum_{s_1 = -1}^{1} \sum_{s_2 = -1}^{1} \cdots \sum_{s_N = -1}^{1} g(s_1s_2)g(s_2s_3)\cdots g(sNs_1)
\]

When we introduce the following matrix:

\[
T = \begin{pmatrix}
    g(1,1) & g(1,-1) \\
    g(-1,1) & g(-1,-1)
\end{pmatrix} = \begin{pmatrix}
    e^{-\zeta + \beta \mu/2} & e^{\beta \mu/2} \\
    e^{\beta \mu/2} & e^{\zeta - \beta \mu/2}
\end{pmatrix}
\]

the summation in Eq. (15) can be expressed in terms of the trace of \( T^N \), which is reduced to the sum of the \( N \)-th power of two eigenvalues of \( T \), i.e.

\[
Z = \exp\left[ -\frac{\beta N}{2} (\mu_A + \mu_B + u_{AA} + u_{AB}) \right] (\lambda_+^N + \lambda_-^N)
\]

where \( \lambda_+ \) and \( \lambda_- \) are solutions of the determinant
where

\[
\lambda_\pm = e^{-\beta \mu /2} \cosh(\zeta /2)(1 \pm \chi)
\]

(19)

Thus, (1/\beta Z)\zeta \partial Z/\partial u gives the average of \(N_{AB}\). Carrying out the differentiation of Eq. (17), we obtain the average number of the AB pairs

\[
\theta_{AB} \equiv \frac{\langle N_{AB} \rangle}{N} = \frac{1}{N} \frac{\zeta \ln Z}{\partial u}
\]

(23)

\[
= \frac{1}{\zeta} \frac{\partial Z}{\partial \zeta}
\]

\[
= \frac{1}{\zeta} \frac{\partial Z}{\partial \zeta}
\]

(24)

This is equivalent to Eq. (11) for \(N = 3\). The value of \(N\) should be sufficiently large such that 1/\(N\) is regarded as zero. Then Eq. (24) tends to

\[
\theta_{AB} = \frac{e^{\beta \mu}}{1/2} \sech^2(\zeta /2)
\]

(25)

This equation provides variations of \(\theta_{AB}\) with \(\zeta\) and \(\beta \mu\).

The expression for \(\theta_{AA}\) is derived here. From the intuitive relations \(N_A + N_B = N\) and \(N_A - N_B = \sum_n n s_n\), we obtain \(N_A = (N + \sum_{n=1}^N n s_n)/2\). When this is inserted into the mass balance, \(2N_A = 2N_{AA} + N_{AB}\), we have

\[
N_{AA} = \left( N + \sum_{i=1}^N s_i - N_{AB} \right) / 2
\]

(26)

From Eqs. (12) and (13), we can derive

\[
\frac{\partial Z}{\partial \zeta} = \frac{1}{\sum_{i=1}^N s_i} \sum_{i=1}^N \sum_{s_i} \sum_{s_{i+1}} \cdots \sum_{s_{N-1}} \sum_{s_N} \left[ N - \sum_{j=1}^N s_j \right] e^{-\beta \mu}
\]

(27)

Combination of Eqs. (26) and (27) gives the expression for the normalized average of \(N_{AA}\)

\[
\theta_{AA} \equiv \frac{\langle N_{AA} \rangle}{N} = 1 - \frac{\partial Z}{N \partial \zeta} \theta_{AB} / 2
\]

(28)

Carrying out the complicated differentiation of \(\partial Z/\partial \zeta\), we obtain

\[
\theta_{AA} = 1 - \frac{1}{2} + \frac{1}{\zeta} \frac{\partial Z}{\partial \zeta}
\]

(29)

where \(t = \tanh(\zeta /2)\). Eq. (29) represents the relation of \(\theta_{AA}\) with \(\zeta\) and \(\beta \mu\).

Fig. 5 shows variations of \(\theta_{AA}\), \(\theta_{AB}\) and \(\theta_{BB}\) with \(\zeta\) at two values of \(\beta \mu\) ((a) and (b)). \(\theta_{AA}\) and \(\theta_{BB}\) are, respectively, decreasing and increasing functions of \(\zeta\), whereas \(\theta_{AB}\) shows a bell shape. There is a domain of \(\zeta\) in which AA, BB and AB coexist. The coexistence is consistent with the experimental results shown in Fig. 2. The peak height of \(\theta_{AB}\) increases with an increase in the value of \(\beta \mu\). This variation is coincident with the expectation that the pair AB is more stable as \(u_{AB} (= u_{AA} - u)\) is more negative. The domain of \(\zeta\) in which AA is rich becomes necessarily larger with an increase in values of \(\beta \mu\). Fig. 5 also shows curves (dotted) calculated from Eqs. (10) and (11) for \(N = 3\). These curves for \(\beta \mu < 0\) are very similar to those for \(N = \infty\), whereas those for \(\beta \mu > 0\) at \(N = 3\), especially of \(\theta_{AB}\), are different from those at \(N = \infty\). The difference is due to the occurrence of complicated arrangements at \(N = \infty\).

The amount of the pair AB has a maximum value at \(\zeta = 0\) (\(\theta_{AA} = \theta_{BB}\)), as is shown in Fig. 5. The maximum amount of \(\theta_{AB}\) is plotted against \(\beta \mu\) in Fig. 6. The value of \(\theta_{AB}\) increases with an increase in \(\beta \mu\), and then tends
to unity. The value of $\theta_{AB}$ at $\beta u = 0$ is 0.5, whereas $\theta_{AA}$ and $\theta_{BB}$ are both 0.25. These values can readily be understood because pairs of AA, BB, AB and BA are generated at a common probability (0.25) for $u_{AA} = u_{BB} = u_{AB}$. The pair AB is predominant at $\beta u > 3$ or $u_{AB} < u_{AA} = 7$ kJ mol$^{-1}$ at 25 °C, whereas it is negligibly small at $\beta u < 3$ or $u_{AB} > u_{AA} = 7$ kJ mol$^{-1}$. In the intermediate domain ($|\beta u| < 3$), the three pairs coexist. The maximum of the experimental values of $\theta_{AB}$ is about 0.25, according to Fig. 2. Thus, the value of $\beta u$ corresponding to $\theta_{AB} = 0.25$ is $-1.1$, or $u_{AB} - u_{AA} = 2.7$ kJ mol$^{-1}$ at 25 °C. Since the pair AA or BB is predominant to the pair AB, it is apt to generate a homo-combination of AA···A or BB···B rather than a hetero-one AB···AB. The long homo-combination leads to the formation of a macroscopic phase. Consequently, the experimental voltammograms exhibit not only desorption waves of A and B from their phases but also the desorption wave of the interactive species, AB.

3. Monte Carlo simulation

It is interesting to look at the phase patterns of distributions of A and B, as has been reported through STM [42,46] and AFM images [48,49]. Since $Z$ represents a canonical average, it does not give any pattern. The technique of generating a theoretical pattern is dynamic Monte Carlo simulation, in which either A or B occupies each lattice site randomly and then is inverted each to the other (A ↔ B) according to the probability of the inversion.

The model of the present simulation is on a two-dimensional hexagonal $n \times n$ lattice with periodic boundary conditions. The closest neighbor, $s_{i,1}$, in Eq. (12) should be read as six closest neighbors. Then the Hamiltonian of a species (A or B) at site ($i, k$) is written by replacing $N$ by 1 in Eq. (12)

$$
H(1) = \frac{1}{2}(\mu_A + \mu_B + u_{AA} + u_{AB}) \\
+ \frac{1}{2}(\mu_A - \mu_B)s_{i,k} + \frac{u}{2}s_{i,k}S_{i,k}
$$

where

$$
S_{i,k} = s_{i-1,k,k-1} + s_{i-1,k,k+1} + s_{i,k+1} + s_{i,k-1} + s_{i+1,k} \\
+ s_{i+1,k}
$$

The probability of a site being occupied by A or B is given by $\exp(-\beta H(1))$. When A ($s_{i,k} = 1$) is replaced by B ($s_{i,k} = -1$), the probability of the occupation is changed from $\exp[\beta (\mu_A - \mu_B) + uS_{i,k}/2]$ to $\exp[-\beta ((\mu_A - \mu_B) + uS_{i,k}/2)]$. Then, the normalized probability of the replacement is expressed by

$$
p = \frac{\exp[-(\zeta + \beta uS_{i,k})s_{i,k}/2]}{\exp[\zeta + \beta uS_{i,k}/2] + \exp[-(\zeta + \beta uS_{i,k})s_{i,k}/2]}
$$

When a random number ranging from 0 to 1 is larger than $p$, $s_{i,k}$ (A or B) is converted to $-s_{i,k}$ (B or A). Otherwise, $s_{i,k}$ remains the same.

The Monte Carlo simulation was carried out by the following processes:

1. by making a memory arrangement for the $n \times n$ two-dimensional hexagonal lattice, onto which A and B are randomly distributed for a given value of $\zeta$;
2. by applying the periodical boundary conditions;
3. by making a numerical table with seven kinds of $p$, corresponding to $S_{i,k} = -6, -4, -2, 0, 2, 4, 6$;
4. by applying the periodic boundary conditions; and
5. by evaluating some thermodynamic values such as $\theta_{AA}$ and $\theta_{AB}$ by averaging the number of pairs.

A typical value of $n$ was 32. The simulation was performed by a computer with a 600 MHz clock. Since each site is surrounded with six sites, the value of $n$ in this model is equivalent to one-third of that in the one-dimensional model.
Fig. 7 shows the dependence of $\theta_{AA}$ and $\theta_{AB}$ evaluated thus on $\beta u$ for $\zeta = 0$. The value of $\theta_{AB}$ increases with $\beta u$ and then reaches a value of 0.55. This is smaller than unity in comparison with the dotted curve for the one-dimensional model. The low value is ascribed to the inevitable presence of AA or BB around AB for any arrangement at large values of $\beta u$. Values of $\theta_{AA}$ for $\beta u > -0.5$ show only a small variation (from 0.22 to 0.38) with $\beta u$. When $\beta u < -0.6$ or $u_{AB} - u_{AA} = 1.4 \text{kJ mol}^{-1}$ at 25 °C, values of $\theta_{AA}$ or $\theta_{AB}$ stochastically take either 0 or 1, corresponding to the lattice occupied with only A or B, respectively. In other words, phase separation occurs to form an A-rich or B-rich domain. Indeed, the standard deviation of $s_{k,\sigma}$ becomes very large at $\beta u = -0.5$, as is shown in Fig. 7 on the left axis.

From the curve of $\theta_{AB}$ in Fig. 7, we estimated the value of $\beta u$ corresponding to the experimental value of $\theta_{AB}$ to be $-0.5$ or 1.2 kJ mol$^{-1}$. This absolute value is 1.4 times larger than the value ($\beta u = -1.1/3$, 3 is the coordination number) from the one-dimensional model. Since the hexagonal arrangement has more degrees of freedoms in the distribution of A and B than the one-dimensional arrangement, it requires more interaction energy to reduce the one-dimensional arrangement.

It is interesting to compare the value of $u$ with the known value of the interaction energy of $-\text{CH}_2 -$ in $n$-alkanes. The latter would be the value of the enthalpy of the $n$-alkanes obtained from the melting points, ca. 1.7 kJ mol$^{-1}$ [60]. The experiment in Fig. 2 was made with a binary SAM composed of 1-hexadecanethiol (HDT) and 3-mercaptopropionic acid (MPA). The difference in the number of methylene groups of HDT and MPA is 13, and hence the difference in the enthalpy is predicted to be $1.7 \times 13 = 22 \text{kJ mol}^{-1}$ if the two species are crystallized. In contrast, the value of $|u|$ obtained from Fig. 7 is 1.24±0.57 kJ mol$^{-1}$. The energy that a methylene site takes is six times larger than the value of $u$ because of the hexagonal configuration. Thus, we estimate $1.24 \times 6 = 7.4 \text{kJ mol}^{-1}$. This is one-third of the energy of enthalpy of crystal $n$-alkanes. The distance of the closest methylene chains in SAMs is controlled by the distance between the atomic distance of the metals, e.g. 0.5 nm for Au(111). On the other hand, the distance of the methylene chains in polyethylene is 0.3 nm for a polyethylene of density 0.9 g cm$^{-3}$. Therefore, the longer separation of methylene groups in SAMs necessarily decreases the interaction energy from the enthalpy of polyethylene.

The value, $\beta u = -0.5$ is close to the instability point ($-0.57$), at which the phase composition is stochastically A or B. This point is equivalent to the temperature, $-10$ °C (298 K × (0.5/0.57)). Therefore, SAMs produced at temperatures less than $-10$ °C may theoretically be composed of either A or B for them to be uncontrollable. In reality, they may be a mixture of macroscopically large domains of A and B.

The simulation was carried out at $\beta u = -0.5$ and $N = 64$ in order to obtain distributions of A and B. An example is shown in Fig. 8, where the total number of A is identical with that of B. Each species is locally aggregated to form various domains for which the size and shape seem to be random. The scanning microscopic observation indicated that a domain was composed of, on average, 50 particles [42]. There are some domains with ca. 50 particles (enclosed with bold line in Fig. 8), which form islands in the sea of counter species. They take an island form in the sea of the counter species.

4. Conclusions

The experimental results [42] have demonstrated not only the appearance of a new wave just at the middle potential of the two peaks of MPA and HDT but also the presence of large domains caused by phase separation. These can be explained by the analysis of the one- and two-dimensional hexagonal models. The new wave is ascribed to the interacting pair AB, which is stabilized with the intermolecular interaction between closest neighbor particles of MPA and HDT. The source of the interaction is due to the affinity of the methylene
groups. From the comparison of the experimental value of the charge with the theoretical molar fraction, we evaluated the net interaction energy of the methylene group of the SAM to be 7.4 kJ mol\(^{-1}\), which is one-third of the value for the crystal \(n\)-alkanes. The relation \(u_{AA} < u_{AB}\) obtained from \(\beta u = \beta (u_{AA} - u_{AB}) = -0.5\) indicates that the AB pair is less stable than the AA and the BB pairs. However, the SAM does not take either the A- or the B-form, but is a mixture of A-islands in a B-sea and B-islands in an A-sea. The AB can be observed at boundaries of phase A and phase B.

References