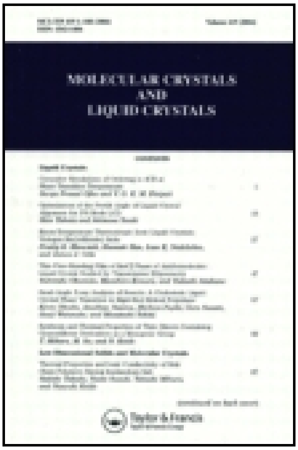

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Thermodynamic Standardization for Highly Photoreactive LB Films Made from Amide Derivative of p-Phenylenediacrylic Acid

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Abstract The thermodynamic concept was introduced in order to elucidate the dynamic flexibility of the amide derivative of p-phenylenediacrylic acid "1" for the formation of its monolayer. The phase transition region appeared in the surface pressure - area isotherms was interpreted in terms of molecular comformational changes between two extreme forms; bent comformation and erect comformation. The LB films prepared at higher temperatures possessed highly oriented and closely packed molecular assembly, as revealed by means of spectroscopy. Even though, the LB films prepared at lower temperatures exhibited a higher photoreactivity.

Keywords Monolayer; Phase transition; LB films; Photoreactive.

INTRODUCTION

Photoactive ultrathin organic films organized by Langmuir-Blodgett method are still having a continued interest with prospect for applications such as optical data storage, LCD and opto-electronic devices. The manipulation of LB films of a series of p-phenylenediacrylic acid derivatives has been discussed in a previous papers [1,2]. Since the concept of hydrogen bonding plays an important rule in the linkage between adjacent spreading amphiphils, therefore the insertion of amide group in p-phenylenediacrylic acid was an aim to manage molecular packing of the compound "1", structured as : $C_{10}H_{21}OCOCH{=}CHC_6H_4CH{=}CHCONHC_6H_4COOH$, by controlling the surface area per molecule thermodynamically, and finally to enhance the photoreactivity of the organized molecular film.

EXPERIMENTALS

The measurements of the surface pressure area isotherm (Π-A curve) were taken on a commercial Langmuir balance (Meßgrätewerk Dr. R. Wobser KG, Lauda). The spreading solution was a 11.9 mg "1", at a concentration of 1×10^{-3}

M, dissolved in tetrahydrofuran:benzene mixture (13:33 by volume) in 25 ml vessel. The sample solution (40 μl) was spread at an initial area of 65 Å^2/molecule onto the subphase. The solvent was allowed to evaporate for 30 minutes. The compression for most measurements was 7 Å^2/(molecule.min). Distilled deionized water was used as subphase. Quartz, hydrophilically treated with KOH-EtOH solution, and CaF_2 were used as substrates. The monolayers were transferred by the LB method. Ultra violet and emission spectra were measured using Shimadzu UV-2500PC and JAS CO FP-777 spectrophotometers, respectively. Photoreaction was performed using a 500 W super-light pressure mercury lamp (Ushio USH-500 D, λ=313 nm). The sample was 10 cm distant from the source.

RESULTS AND DISCUSSION

Monolayer Formation

FIGURE 1 shows the surface pressure-area isotherms measured at different temperatures at the water surface. It is clear that each isotherm possesses a transition between two different phases are to be discussed later. The relation between the transition onset pressure Π_{tr} and the temperature of each isothermal process T is represented in FIGURE 2. As shown in the plot, the data fit well the parabolic equation

$$\Pi_{tr} = \Pi_{inf} + C\,(T - T_{inf})^2 \qquad (3.1)$$

where Π_{inf} = 9.1 mN/m, T_{inf} = 299.1 K and C = 4.6498 x 10^{-5}.mN m^{-2} k^{-2}.

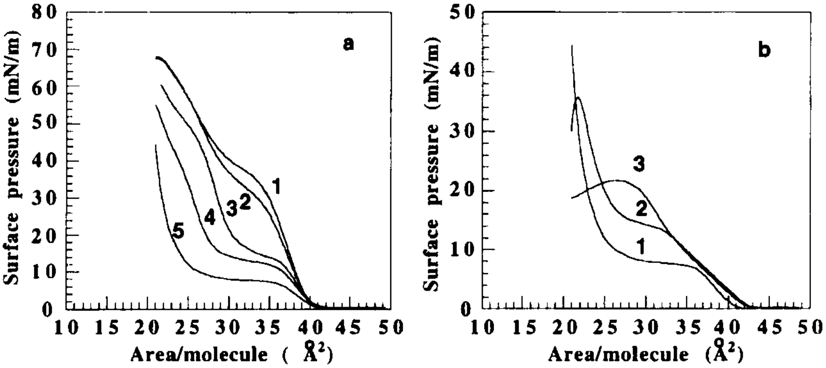

FIGURE 1 Temperature dependence of the Π-A isotherms of "1" at the air-water interface. a) 1:2.4, 2:4.4, 3:14.7, 4:19.9, 5:26.1 °C. b) 1:26.1, 2:38.5 3:41.6 °C.

The phase transition region appearing in the Π-A isotherm indicates that a molecular reorganization and comformational change is taking place within the monolayer [3,4]. This behavior may be explained by two different regimes depending on the temperature as follows: At low temperatures and at zero surface pressure, due to the strong surface tension the molecule sticks rigidly in a strained bent conformation on the aqueous substrate with two polar groups (carboxyl and ester groups) being in touch with the subphase surface leaving the in between portion remaining out. The terminal alkyl chain keeps preferentially in a tilted alignment with the normal to the surface. Once the compression process starts, the two polar groups are directed to each other in a hard compressible fashion that expresses by the higher liquid expanded region. That is to say, the molecule suffers a close-packed bent comformation seen by the model sketched in FIGURE 3b. Then, the sharp inflection at the kink region of the isotherm is an evidence that a molecular reorganization to the erect comformation takes place because the weaker polar group (ester group) is abruptly forced out of the interface and a partially expanded but rigid monolayer was finally formed. Actually, such comformational changes dominate within the temperature range 2-15 °C with an accompanied gradual lift shift of the average molecular area and less sharpness of the transition region. Further increasing in the temperature causes a conversion of the phase transition from the regime mentioned above to

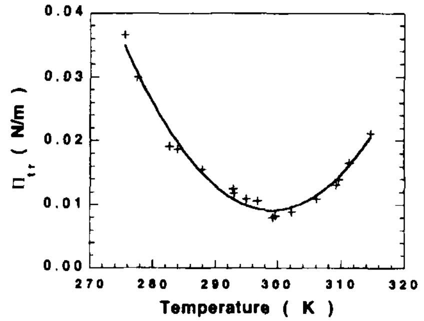

FIGURE 2 Π_{tr} vs T relationship. Solid line is the parabolic fit of the experimental data.

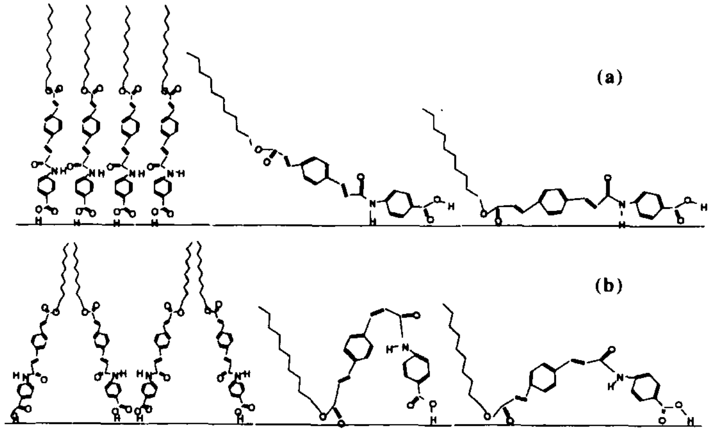

FIGURE 3 Schematic diagram of the phase changes of the compound "I" at the air-water interface. (a) bent to erect comformation at high temperatures. (b) bent to close-packed bent to erect comformation at lower temperatures.

another one that the molecule will suffer a comformational change from the bent (but not the close-packed) comformation to the erect comformation. In this case, the three different polar groups are all immersed in the aqueous because of the lower surface tension of the subphase. So to speak, it is impossible for the close-packed bent comformation to occur since there is a strong and a significant steric hindrance among these tree polar groups. Therefore, above a comparatively short expanded region the molecules are flexible and compressible enough to stand under compression up gradually starting from the alkyl chain side. At the end of the transition region the monolayer becomes condensed but more fluid in an erect comformation (see FIGURE 3a.).

It is worthmentioning that the closed-packed erect comformation was attained at the temperature 26 °C which is the inflection point of the curve shown in FIGURE 2 , above which all features were recovered except that the collapse pressure was effectively decreased. In this case, the work done by the system for bringing the molecule from the bent comformation, against the strong hydrogen bonding formed by the amide group to retain water at such higher temperatures, into erect comformation increases. Besides, the lateral cohesion between adjacent alkyl chains diminishes under the influence of the thermal agitation forcing the molecules to rotate around their long chain axes. Such effect leads the molecular structure to collapse at lower surface pressures and the monolayer is no longer could be formed above 36 °C. It should be pointed out that the bent-to-erect comformation have been confirmed for some spin-labeled probes such as stearic acid nitroxides, and was termed as isotherm reversal [5].

To go further into the in-depth study of the dynamics of "1" molecular system, it was necessary to determine the thermodynamic state functions (such as the molar enthalpy change, ΔH, and the molar internal energy change, ΔU of the system) in the evaluation of the stability of the thermodynamic equilibrium of the different molecular comformations discussed before.
For the two dimension analogue of the Clausius-Clapeyron equation [6,7] we may write these two equations:

$$\Delta H = T\,\Delta A\,(d\Pi_{tr}/dT) \qquad (2)$$

$$\Delta U = \Delta H - \Pi_{tr}\,\Delta A \qquad (3)$$

Where ΔA is the difference in the molecular area within the transition region.

Judging from the results summarized in TABLE 1, The intermolecular interactions can be estimated from the value of molar internal energy as follows: At very low temperature (T = 2.2 °C), where the aqueous substrate is extremely viscous, the carboxyl head groups join together in a strong hydrogen bonding. Therefore, a much work should be done by the system to convert the molecule from the bent to the sharp close-packed bent comformation and finally to the erect comformation. Such comformational change most likely requires an absorption of energy that can be divided between the lateral cohesion between the adjacent alkyl chains (500 cal/mol-10 CH_2) [7] and the remaining ca. 3800 cal/mol for the formation of the carboxyl groups hydrogen bonding. The monolayer is most likely rigid under such forces affecting the two extreme parts of the molecules. As the temperature increases the molar heat of transformation decreases and accordingly the net absorption energy starts at a temperature of ca. 15 °C to decrease significantly. This means that the hydrogen bonding between carboxyl group as well as the lateral cohesion between the alkyl chains start to diminish and a new ,but weaker, hydrogen bond is to be born between the adjacent amide groups. Moreover, a repulsive hydration force may arise between any two neighboring carboxylic acid head groups [4], preventing the irreversible adhesive contacts between these groups. At a moderately higher temperature the molecule absorbs less energy to pass from the bent to erect comformation and becomes more fluid and compressible. The condensed monolayer is therefore thermodynamically stable with an ultimate shrinkage in the area per molecule at the inflection temperature shown by FIGURE 2.

TABLE 1 Evaluation of the thermodynamic state functions and molecular parameters of the monolayer at the transition region.

T (°C)	Π_{tr} (mN/m)	ΔA ($\AA^2$)	ΔH (cal/mole)	ΔU (cal/mole)
2.4	36.6	6.5	5646.3	5303.8
4.4	30.0	6.5	5204.3	4923.6
9.5	19.2	6.5	4045.6	3866.0
10.8	18.7	5.5	3167.2	3019.1
14.7	15.5	6.5	2817.6	2672.6
19.9	11.8	9.5	2254.7	2093.3
21.9	10.9	11.5	1839.5	1659.1
23.7	10.6	12.5	1117.6	926.9
26.1	8.0	13.0	-	-
26.5	8.3	12.8	-	-
29.1	8.9	11.0	1401.9	1261.0
33.0	10.9	9.3	2687.0	2541.1
36.0	13.1	7.2	2994.5	2858.8
36.4	13.9	7.0	3031.1	2891.1
38.2	16.5	4.0	2042.2	1947.2
41.6	21.1	3.0	1978.2	1887.0

Multilayer Formation

The manipulation of LB films at the air-water interface under the condition mentioned above has been attempted. The LB films prepared at temperatures below 15 °C possessed Y-type transfer, which was independent on the substrate nature, with a transfer ratio close to unity. Whereas at temperatures of about 20 °C and above the LB films were of either Z- or X-type using quartz or CaF_2 substrates, respectively. In the later case the molecules were packed and oriented, as revealed by the more intense absorption spectra shown by FIGURE 4(a). Even though, the former LB films exhibited higher photoreactivity as indicated by the relation between the normalized absorption intensity, at the peak position, and the irradiation time illustrated in FIGURE 4(b). More details concerning the criteria of photoreactivity of LB films manipulated at the conditions mentioned above will appear elsewhere [8].

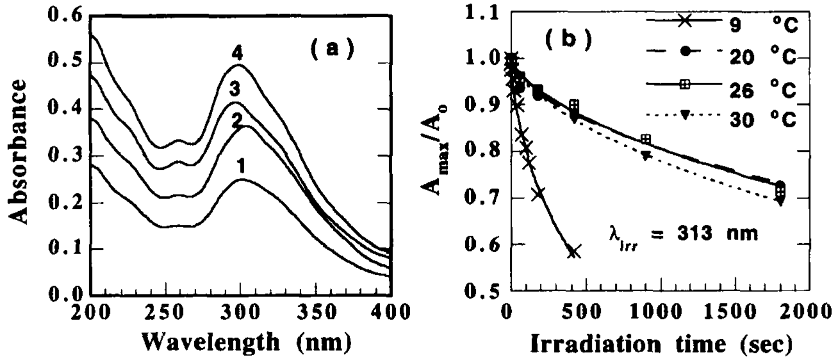

FIGURE 4. (a) Absorption spectra of LB films (14 layers) prepared at 1:9; 2:15; 3:20; 4:26 °C. (b) Time decay profiles of the normalized absorption maximum intensity of LB films prepared at different temperatures

CONCLUSION

The monolayer formation of the "1" molecules at the air-water interface has been investigated at different temperatures. Three types of molecular comformations were suggested for the description of the phase transition region. The thermodynamic concept was utilized to interpret such comformational changes and intermolecular interactions. The existence of amide group was shown to play a significant role in controlling the phase transition phenomenon at the air-water interface through hydrogen bonding concept. The LB films manipulated at low temperatures exhibited higher photoreactivity than those manipulated at temperatures above 15 °C, although the later possessed more packed and oriented molecular structure, as revealed by spectroscopy and photolysis.

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