Langmuir-Blodgett Thin Film Characterization of Two Organic Compounds

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Abstract
Molecular behaviours of two compounds, namely, p-phthalimidobenzoic acid (FIBA) and (N-phthalimido)-p-aminobenzoic acid (FIABA) molecules have been investigated on air-water interface using their isotherm graphs. These compounds were also used for the fabrication of LB thin films onto a glass and quartz substrates. These films were then scanned by an Atomic force microscopy (AFM) for the deposition properties. The optical properties are studied using UV-visible spectroscopy. $\pi \rightarrow \pi^*$ transitions was occurred and the absorption of the FIBA and FIABA LB films against the number of layers showed a linear behaviour. Preliminary results show that these compounds are well-organized at the air-water interface and are suitable materials to produce with the transfer ratio of over 0.95 uniform LB films.

Keywords: *Phthalimides, LB thin films, atomic force microscopy, UV-visible spectroscopy*

İki Organik Bileşenin Langmuir-Blodgett İnce Film Karakterizasyonu

Özet
P-fitalimidobenzoik asit (FİBA) ve (N-fitalimido)-p-aminobenzoik asit (FİABA) olarak adlandırılan iki bileşiğin moleküler davranışları, bu bileşiklere ait izoterm grafikleri yardımıyla hava-su ara yüzeyinde incelendi. Bileşikler aynı zamanda cam ve kuvars alttaşlar üzerinde LB ince filmler depolamak için kullanıldı. Atomik kuvvet mikroskobuyla taranarak filmlere ait depolama özellikleri elde edildi. UV-görünür bölge spektroskopisi yardımıyla filmlerin optik özellikleri çalışıldı. $\pi \rightarrow \pi^*$ geçişleri oluştu ve aynı zamanda FİBA ve FİABA LB filmlerin soğurma şiddetinin tabaka sayısıyla çizgisel olarak değiştiği gözlendi. Elde edilen sonuçlar bu bileşenlerin hava-su ara yüzeyinde iyi organize olduklarını ve 0,95'in üzerindeki transfer oranıyla düzenli LB film ince film üretimi için uygun olduklarını gösterdi.

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Anahtar kelimeler: *Fitalimitler, LB ince filmler, atomik kuvvet mikroskopisi, UV-görünür bölge spektroskopisi*

1. Introduction

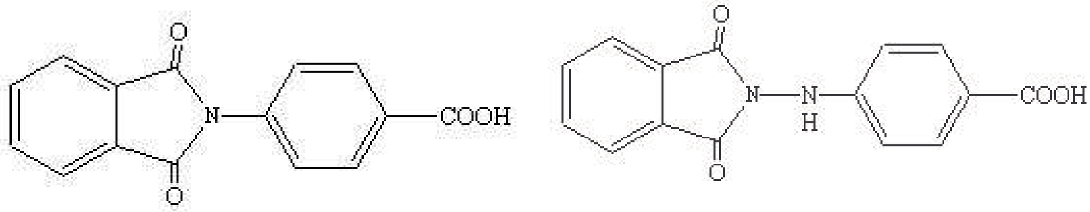
Ultra-thin films are quite important in the nanoscale physics because of their potential applications in fundamental science and technology [1-4]. Many thin film techniques e.g. spin coating, sol-gel and solvent castings have been used to grow organic thin films on the solid substrate. Langmuir-Blodgett (LB) thin film deposition technique is also suitable method to produce organic thin films at nano-scales. This method makes it possible to prepare functional ultra thin films with a controlled thickness at a molecular level.

Actually there exist a number of different organic LB film materials. Here we investigated phthlamide derivatives as LB films. These materials have potential application in many different fields, including, chemistry, medical chemistry, physics etc. Early studies with these materials and their derivatives were carried out in medicine and researchers examined their hypolipidemic activity. The studies with these materials were about their antimicrobial activity, antiandrogen, and other agents for treating tumour necrosis factor. It was found that, using some phthalimide derivatives toxicity of some tumours can be decreased [5] and also some of their derivatives can be used against HIV cells [6]. Some crystals of phthalimides are very suitable as an efficient frequency doubler and optical parametric oscillator due to their high second-harmonic generation (SHG) conversion efficiency [7].

In this work, FIBA and FIABA molecules were fabricated as the thin films using LB film method. Produced films were characterized by the UV-visible and the AFM techniques.

2. Experimental Details

Chemical structures of the FIBA and FIABA which were characterized are shown in Fig. 1 (a) and (b), respectively. For the obtaining isotherm graphics, both materials were dissolved in a dimethyl sulfoxide (DMSO) and chloroform mixture with a concentration of 3 mg/ml. Surface pressure of monolayers were measured by the Wilhelmy-plate method. Different amounts of solutions with the same concentrations were used to obtain the deposition pressure values by using the isotherm graphs as in Fig. 2 (a) and (b) and deposition pressures were determined using these two graphs as 15 mN/m and 9 mN /m for FIBA and FIABA, respectively. A Z-type LB film was than prepared using these pressure values with NIMA LB trough type 622 (Coventary England) with the area 1200 cm^2 and than different number of layers FIBA and FIABA LB films were deposited onto optically flat hydrophilic glass and quartz substrates.



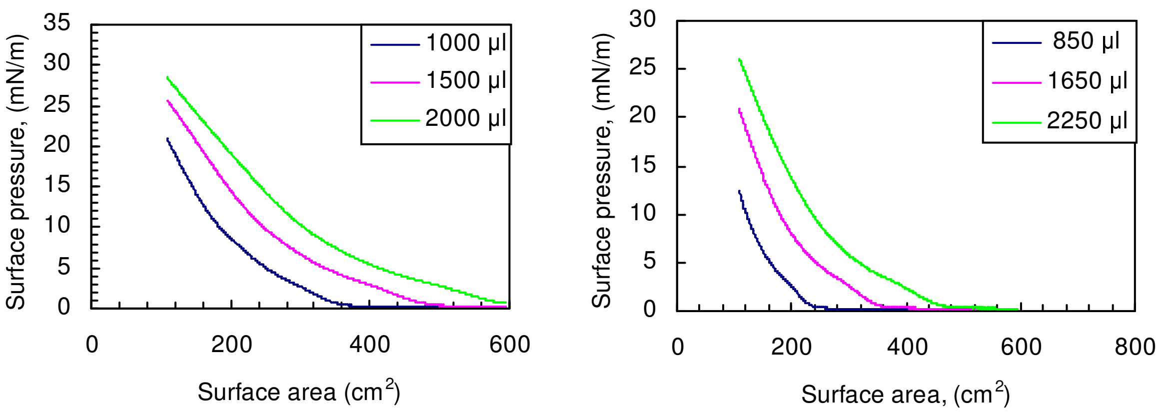
(a) (b)

Figure 1. The chemical structure of (a) p-phthalimidobenzoic acid (FIBA) and (b) (N-phthalimido)-p-aminobenzoic acid (FIABA).

Characterization of these LB films was made by using its UV-visible spectroscopy and AFM scan. We obtained the needed LB films at different number of layers, using a solution concentration of 3 mg ml^{-1} for both materials. Absorption spectra of the FIBA and FIABA films deposited on quartz substrates were recorded using a UV-visible spectrophotometer (Varian CARY 50 spectrophotometer). The AFM analyses of these materials, 15 layer LB films were deposited on the glass substrates and using these films it was performed in a contact mod. A standard silicon nitride tip was used to obtain the images.

3. Results

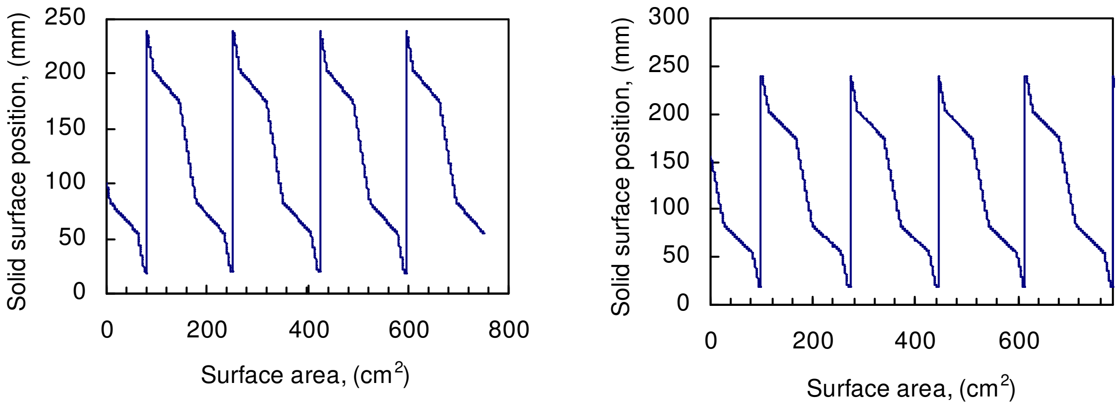
Isotherm graphs which were recorded at the room temperature are given in Fig. 2 (a) and (b) for FIBA and FIABA materials, respectively. Using these graphs, a deposition pressure values were determined as 15mN/m for FIBA and 9 mN/m for FIABA and LB film was deposited on the glass substrate at room temperature on a NIMA LB trough.



(a) (b)

Figure 2. Isotherm graphics of (a) FIBA and (b) FIABA monolayer

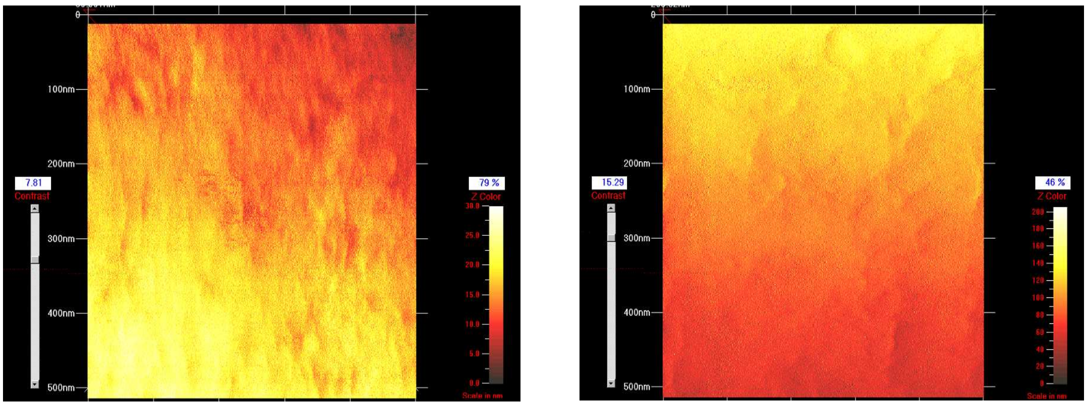
Fig. 3 (a) and (b) show the change of the area during the deposition for 9 layers of FIBA and FIABA LB film. Graphs show that, the reduction of the areas are the same and the transfer ratio is calculated over 95 %. This indicates that, similar amounts of molecules are deposited on the glass substrates and this is a proof that we can obtain uniform and stable LB films.



(a) (b)

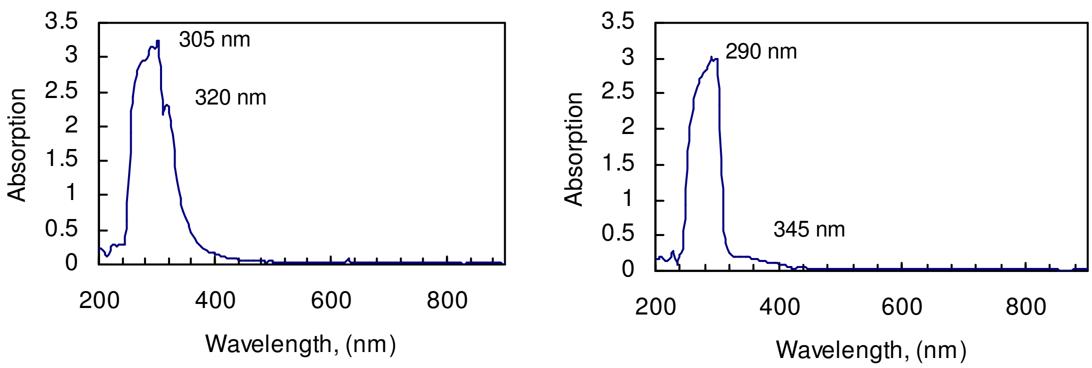
Figure 3. LB film deposition graphics of the (a) FIBA and the (b) FIABA multilayers onto the glass substrate. LB film deposition graph of FIBA.

Results were supported with the AFM pictures shown in Fig. 4 (a) and (b). Surface image of LB films for two different materials; deposited onto optically flat hydrophilic glass substrates were obtained using AFM in the contact mode. These images show as smooth and uniform. There are no big voids or fragment on their surfaces. Surface morphologies of these film are very similar to the N-dodecylphthalimide LB films [7] and fluorine containing poly(amide–imide)s LB films [8].



(a) (b)

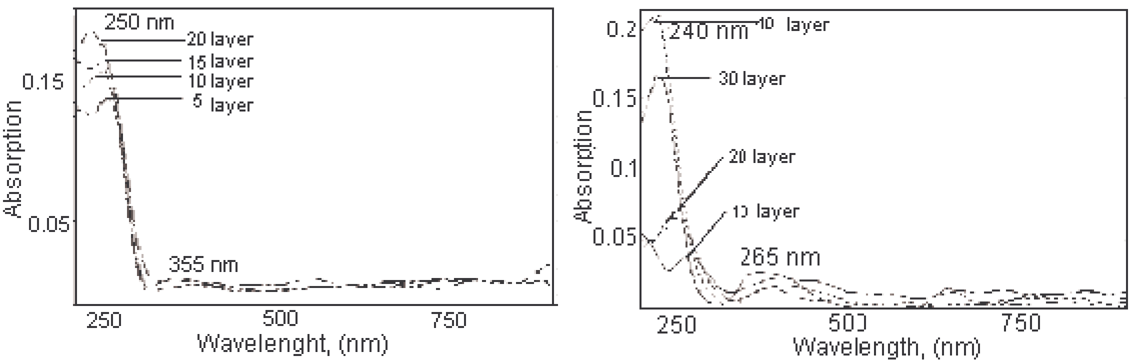
Figure 4. Two dimension AFM image of 15 layer (a) FIBA (b) FIABA LB thin film



(a) (b)

Figure 5. UV-visible spectrums of the (a) FIBA and (b) FIABA solution

Optical absorption spectra were recorded in the wavelength range of 200–800 nm. Fig. 5 (a) and (b) show typical UV–visible absorption spectra of Phthalimide derivatives in the chloroform solutions. The solutions absorption spectra exhibit absorption bands at 305 nm and 320 nm for FIBA and at 290 nm and 345 nm for FIABA. Generally, phthalimide and their derivatives exhibit UV–visible spectra with a strong absorption regions around 200–400 nm corresponding to the $\pi \rightarrow \pi$ transition of the molecule backbone [9-11]. Fig. 6 (a) and (b) shows UV-visible absorption spectra of LB films of FIBA and FIABA molecules deposited on quartz substrates with different number of layers, respectively. The spectra for the different number of layers are characterised with the maximum in about 250 and 355 nm in Fig. 6 (a) and 240 and 265 nm in Fig. 6 (b). These results are characteristic for phthalimide derivatives as a film and a bulk material and are in good agreement with ones obtained LB films of Fluorine containing poly(amide–imide)s [8] and as the bulk materials with N-(3-nitrophenyl)phthalimide [12] and phthalimide dyes [13].



(a) (b)

Figure 6. UV-visible spectrums of the (a) FIBA and (b) FIABA LB films

Using UV-visible spectroscopy, material amount which was deposited on the substrates can investigated according to number of layers. In literature, absorbance of the thin films of the materials changes linearly according to the Lambert-Beer law [14]. Fig. 7 (a) was plotted using Fig. 6 (a) for FIBA thin films and it can be seen that this graphic absorbance changes linearly. Similar behaviour was showed for FIABA in Fig. 7 (b) was plotted using Fig. 6 (b). The linear relationship between the absorption intensity and the number of layers indicates that there are fairly constant transfer ratios during sequential dipping of the slide through the LB monolayer of both materials. These results are good agreement with literature for the phthalimide LB films [8].

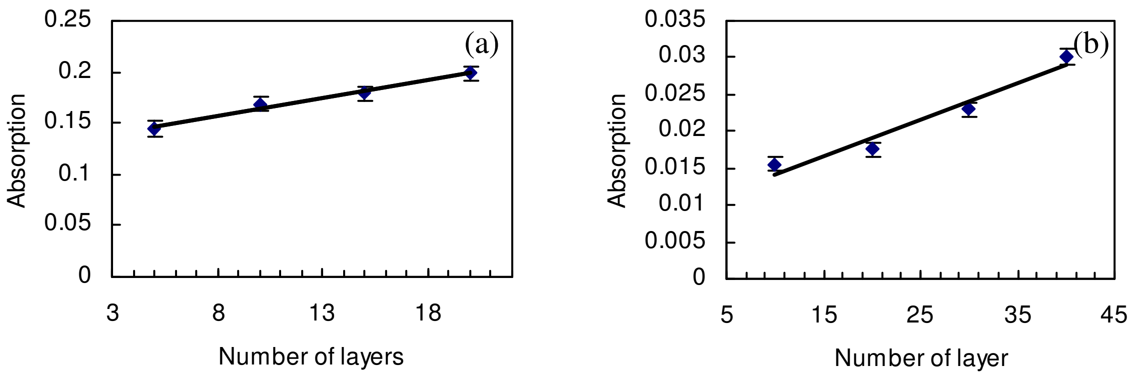


Figure 7. Absorption graphs of the (a) FIBA and (b) FIABA LB films via number of the layers.

4. Conclusion

From the analyses of isotherm graphs, surface pressure of deposition was chosen 15mN/m for FIBA and 9 mN/m for FIABA. The transfer ratio was established over 95 % for LB films of both materials. UV–visible absorption spectra of FIBA and FIABA LB films showed a good linear relationship between the absorption intensity and the number of layers, indicating a fairly constant transfer ratio with a uniform deposition. The resultant smooth and uniform surface morphologies indicate that, these materials are very well ordered on the water surface. The thin film deposition technique allowed us to fabricate usable organic LB films for potential application.

References

[1] Roberts G., **Langmuir-Blodgett Films**, Plenum Press, New York, 1990.
[2] Liz-Marzan L.M., Kamat P.V., **Nanoscale Materials**, Kluver Academic Publishers, New York, 2003.
[3] Ding X. and Xu H., **Thin Solid Films**, 338, 286-290, (1999).
[4] Liang B.J., Zang Y., Yuan C.W., Wei Y., Wengi C., **Sensors Actuators B**, 46, 24-29, (1998).
[5] Miyachi H., Ogasawara A., Azuma A., Hashimoto Y., **Bioorganic & Medicinal Chemistry**, 5, 2095-2102, (1997).
[6] Krištafor, V., Raić-Malić, S., Cetina, M., Kralj, M., Šuman, L., Pavelić, K., Balzarini, J., De Clercq, E. and Mintas, M., **Materials Letters**, 25, 2269-2276, (2006).
[7] Evyapan, M., Çapan, R., Namli, H., Turhan, O., Stanciu, G.A., **Materials Letters,** 60, 2371-2374, (2006).
[8] Onah E.J., Oertel U., Hubler L., Voigt D., Froeck C., Komber H., Voit B.I., Lunkwitz K., **European Polymer Journal**, 39, 127–134, (2003).
[9] Mikroyannidis J.A., Tsai L.R. Chen Y, **Synthetic Metals**, 159, 1195-1201, (2009).
[10] Chang C.J., Tsai M.H., Kao P.C., Tzeng H.Y., **Thin Solid Films**, 516, 5503-5507, (2008).
[11] Behniafar H., Abedini-pozveh A, **Polymer Degradation and Stability**, 96, 1327-1332, (2011).
[12] Ravindra H.J., Suresh Kumar M.R., Rai C., Dharmaprakash S.M., **Journal of Crystal Growth**, 294, 318–322, (2006).
[13] Dierschke F., Jacob J., Mullen K., **Synthetic Metals**, 156, 433–443, (2006).
[14] Koenig J.F., Martel D., **Thin Solid Films**, 516, 3865-3872, (2008).