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Host-Guest Sensing Interactions of Calixarene-Entrapped Para-Aminobenzoic Acid Using the Langmuir Technique

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ABSTRACT

Calixarenes are frequently studied as the host supramolecule in drug carrier applications. The ability to encapsulate and control drug delivery is due to their unique structures with a hydrophobic upper rim and a hydrophilic lower rim. Para-aminobenzoic acid (PABA) is a drug used as the main ingredient in sunscreen products with photoallergic contact dermatitis effects. This study has been motivated by the necessity of developing a PABA sensor even at a deficient concentration. In this work, the uses of two calixarenes, calix[4]arene (C4) and calix[6]arene (C6), in entrapping the PABA drug have been studied using the Langmuir technique. In the Langmuir-Blodgett trough, calixarenes in solution form were prepared and spread on the subphase to form the Langmuir monolayer. The formation of Langmuir films by C4 and C6 has been investigated based on the surface pressure-area (Π-A) isotherm and surface potential-area (ΔV-A) isotherm recorded using Langmuir apparatus KSV 2000 System 2. The differences and changes of the isotherms with the presence of para-aminobenzoic acid (PABA) in the subphase during the formation of Langmuir films have been observed and studied. The interactions between calixarenes and PABA have been shown by the effective dipole moment ($\mu_\perp$) of the calixarene-PABA complexes calculated based on the ΔV results using the Helmholtz equation. Host-guest interaction shown by the sensing of PABA by calixarenes happens most probably at the lower rim of calixarenes due to the amphiphilic property of calixarenes. The findings of this study can be applied to the potential application of drug sensors using C4 and C6.

Keywords: Calixarenes, drug sensor, host-guest, isotherm, Langmuir, PABA

1. INTRODUCTION

The host-guest mechanism of calixarene-entrapped para-aminobenzoic acid is investigated in this study. Host-guest interaction as a chemical complex formation of at least two molecules held together as a structure, with a macrocyclic host molecule accommodating a guest molecule, is widely applied in different fields, including drug sensors for medical and pharmaceutical benefits (Wagner, 2020; Gontero et al., 2017). For example, cyclodextrins and calixarenes are macrocyclic structures that have been explored extensively as sensing materials. Due to their distinctive structures and qualities, both calixarenes and cyclodextrins are finding significant application in numerous industries. However, being the third generation of supramolecular compounds following crown ethers and cyclodextrins, calixarenes with a better molecular binding ability possess benefits and advantages (Wong et al., 2022). Calixarenes are supramolecules shaped like a cup with a hydrophobic upper rim and a hydrophilic lower rim, as shown in Figure 1 (McMahon et al., 2003).

Figure 1. Chemical structure of (a) a typical C4 and (b) the PABA molecule

Due to their outstanding structure, calixarenes are considered extraordinary macrocycles with good drug carrier properties (Fan & Guo, 2020). This study of calixarenes as host molecules has been motivated by its numerous applications in nanosensors. (Kurniawan et al., 2020; Liu et al., 2020; Shah, 2020). However, the use of calixarenes as a drug sensor is still a relatively novel concept. Despite previous research regarding the application of calixarenes in various fields, studies for sensing drugs by calixarenes via host-guest interaction using the Langmuir technique are relatively low. In this research, calix[4]arene (C4) and calix[6]arene (C6) have been chosen as sensing materials due to the structural features for trapping guest molecules (Español & Villamil, 2019; Kumar et al., 2017; Baklouti, 2007). C4 owns a stable and unique structure, whereas C6 has a larger and more flexible structure (Becher & Schaumburg, 2013; Lo & Wong, 2008).

Para-aminobenzoic acid or known as 4-aminobenzoic acid (PABA), as shown in Figure 1, is a vitamin commonly used as the main ingredient in the sunscreen product due to its ability to absorb ultraviolet (Drozd et al., 2018; Singh et al., 2021). However, PABA has side effects, including photoallergic and allergic contact dermatitis (DeLeo, 2018). Thus, the development of a PABA drug nanosensor, even at a very low concentration, is necessary.

In this study, PABA was aimed to be detected by calixarenes via host-guest interaction at the air-water interface using the Langmuir technique. The formation of Langmuir films could be applied to measure the host-guest interaction (Jurak et al., 2021; Yang et al., 2017). The application of calixarenes by forming a Langmuir monolayer in the sensor field due to its insolubility in water and solubility in a volatile solvent is worth studying (Razali et al., 2021; Supian et al., 2021; Azahari et al., 2014). C4 and C6 were prepared in the form of solution and spread on the subphase in the Langmuir-Blodgett trough. The formation of C4 and C6 monolayers was studied based on the surface pressure-area (Π-A) isotherm and surface potential-area (ΔV-A) isotherm. The host-guest mechanisms of calixarene-entrapped PABA, which refer to calix[4]arene-PABA (C4-PABA), and calix[6]arene-PABA (C6-PABA) complexes, were indicated by the changes of the isotherms due to the presence of PABA in the subphase. The effective dipole moment ($\mu_\perp$) calculated using the Helmholtz equation showed host-guest interaction between calixarenes and PABA at different concentrations. This may be applied for the drug sensor application using C4 and C6. Moreover, the sensing of PABA is believed to head toward the development of PABA drug sensors in the medical and pharmaceutical fields.

2. MATERIALS AND METHODS

Calixarenes with four and six phenolic units, calix[4]arene-25,26,27,28-tetrol (C4) and calix[6]arene-37,38,39,40,41,42-hexol (C6), were used as sensing materials. The tested drug PABA purchased from Bendosen was used as guest molecules. 0.2 mg/ml of C4 and C6 solution were prepared using C4 and C6 powder purchased from Aldrich and chloroform solvent. The

Langmuir-Blodgett (LB) trough was cleaned using chloroform and rinsed with deionised (DI) water, whereas the barriers and the KSV SPOT reference plate were cleaned using ethanol. Then, the subphase was prepared by pouring the subphase solution gently on the trough until rising above the trough's border. A filter paper as the surface pressure sensor was hung and adjusted until suspended at the air-water interface. Then, 1900, 2000, 2100, and 2200 μl of C4 were spread on the subphase of DI water separately. The decision of using such a high volume of C4 was due to the stability performance shown by the monolayer with the demonstration of two-dimensional (2-D) gaseous, liquid, and solid phase transition based on the results of Π-A isotherm when using this volume range. Before starting the measurement, 15 minutes were allocated for the evaporation of chloroform to remain monolayer at the air-water interface, with their hydrophobic and hydrophilic regions, as shown in Figure 2.

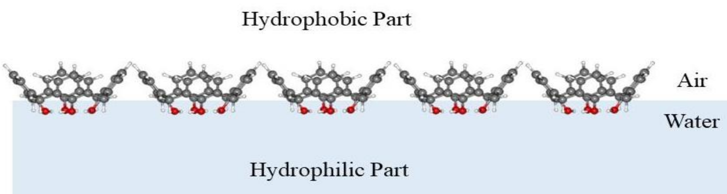

Figure 2. Schematic diagram of C4 with the hydrophobic and hydrophilic regions

The Π-A and ΔV-A isotherms were measured and recorded simultaneously by the Langmuir apparatus, KSV 2000 System 2, together with the KSV SPOT device with an accuracy of ±0.01mN/m and ±1mV, respectively. The vibrating plate of SPOT was placed around 2 mm above the subphase, whereas the reference plate connected to the SPOT was immersed in the subphase, as shown by the setup of the Langmuir apparatus in Figure 3. The steps were then repeated to form the C6 monolayer using the C6 solution.

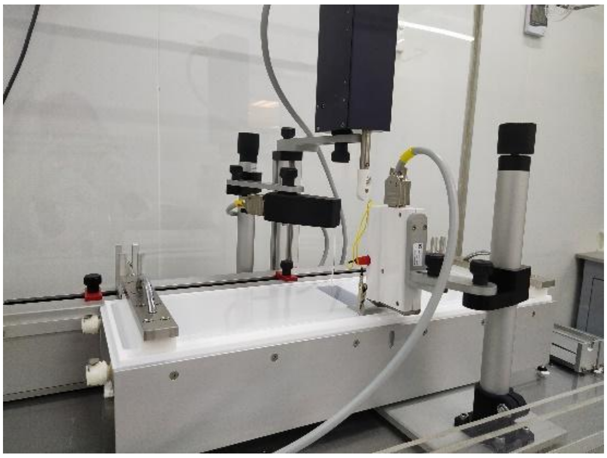

Figure 3. The setup of the Langmuir apparatus

Based on the results of Π-A isotherm, the formation of C4 and C6 monolayers using 2100 μl was considered stable. Thus, 2100 μl of C4 was spread on the subphase with the presence of PABA at different concentrations to form the C4-PABA monolayers. Different concentrations of PABA solution in the range from 0.015 mg/ml to 0.085 mg/ml, with an increment of 0.005 mg/ml, were used as subphases. Then, the steps were repeated to form the C6-PABA monolayer using the C6 solution. Several forms of PABA including ions with the NH_3 cation, COO anion, and neutral molecules that acted as guest molecules were used in this study as shown in Figure 4 (Mirzaei et al., 2012).

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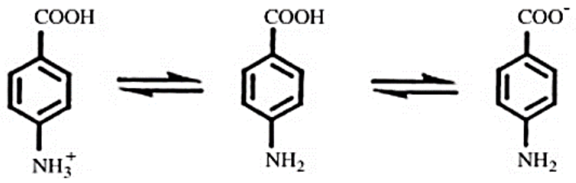

Figure 4. The forms of PABA in aqueous solution. Adapted with permission from "Determination of para-aminobenzoic acid (PABA) in b-complex tablets using multivariate curve resolution-alternating least squares (MCR-ALS) method by Mirzaei et al. (2012). Copyright 2012 by Elsevier"

On the other hand, the $\mu_{\perp}$ as shown in Eq. 1 was calculated by reshuffling the Helmholtz equation after obtaining the results of ΔV-A isotherm.

$$\mu_{\perp} = 2.654\ \Delta VA \qquad \text{(Eq. 1)}$$

where $\mu_{\perp}$ is in D, ΔV is in V and A is in nm^2.

3. RESULTS AND DISCUSSION

3.1. Surface Pressure-Area (Π-A) Isotherm of Calix[n]arene and Calix[n]arene-PABA

Using the Langmuir technique, the behaviour and interaction between molecules at the air-water interface could be studied for the sensor application based on the measurement of Π and ΔV. The Π-A isotherm has been used to monitor the changes in the physical state of the C4, C6, C4-PABA, and C6-PABA monolayer film upon compression by the barriers. The Π-A isotherm for 2100 μl of C4 and C6 with their complexes of the targeted PABA with the lowest concentration detected, which are 0.035 mg/ml and 0.020 mg/ml, respectively have been shown in Figure 5. Besides, the mean molecular area (A_0) of C4-PABA and C6-PABA with different concentrations shown in Table 1 are determined by interpolating the steepest part of the curve to the horizontal axis.

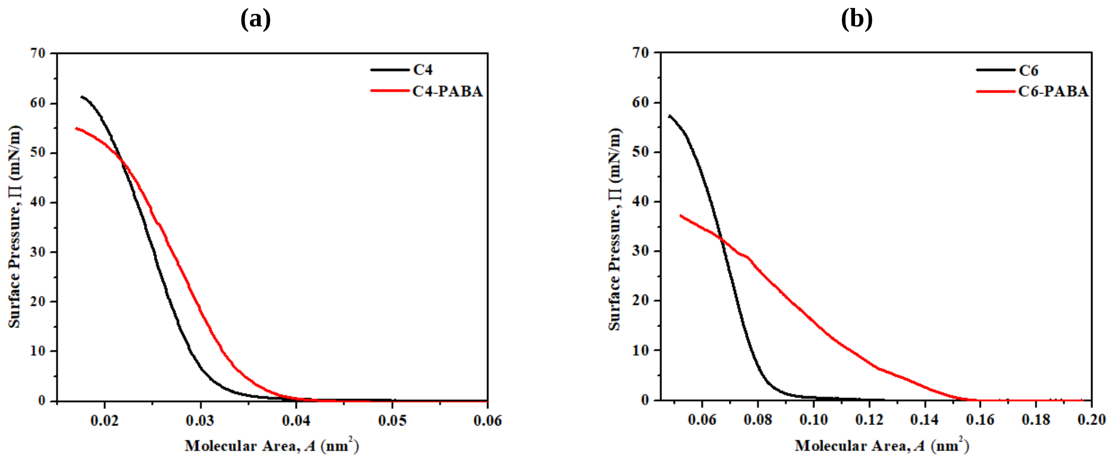

Figure 5. (a) Π-A isotherm of C4 with C4-PABA and (b) C6 with C6-PABA

As shown in Figure 5, the C4, C6, C4-PABA, and C6-PABA Langmuir films are in a 2-D solid phase, which is a highly condensed condition approximately at 30 mN/m, 25 mN/m, 30 mN/m, and 20 mN/m respectively. At this phase, the isotherm curve is the steepest since the molecules are packed together (Singh, 2022). The Π-A isotherm for C4 and C6 with their PABA complexes has proved the host-guest interaction between the macrocyclic host and guest molecules. When PABA solution is used as the subphase, shifting to the right-hand side is shown obviously by the Π-A isotherm graph due to the larger complex sizes of C4-PABA and C6-PABA. The increase of A_0 shown in this study is in good agreement with the previous research regarding the existence of interaction between drugs with monolayer using the Langmuir technique (Wang & Zhu, 2021). However, there is a kink point of A_0 at the PABA concentrations of 0.065 mg/ml and 0.045 mg/ml for C4 and C6, respectively. At those critical concentrations, the A_0 of C4-PABA and C6-PABA reach maximum values after the increase in A_0 with the presence of PABA, which is 0.0468 nm^2 and 0.1414 nm^2, respectively. By the way, the values of A_0 are getting smaller after those critical concentrations due to the closer packing density in a higher concentration condition as reported by previous research made (Ruwoldt, 2020; Hua & Angle, 2013).

Table 1. The A_0 of C4-PABA and C6-PABA

Concentration (mg/ml)	**A_0 of C4-PABA (nm^2)**	**A_0 of C6-PABA (nm^2)**
0	0.0305	0.0815
0.015	-	0.0778
0.020	-	0.1302
0.025	-	0.1373
0.030	0.0240	0.1293
0.035	0.0348	0.1223
0.040	0.0365	0.1293
0.045	0.0371	0.1414
0.050	0.0389	0.1190
0.055	0.0402	0.1248
0.060	0.0396	0.1098
0.065	0.0468	0.0635
0.070	0.0368	-
0.075	0.0381	-
0.080	0.0403	-
0.085	0.0302	-

According to the Π-A isotherm, the C4 is able to detect PABA from the range of 0.035 mg/ml to 0.080 mg/ml, whereas the detectable concentration range for C6 is from 0.020 mg/mL to 0.060 mg/mL. Further increment or reduction of concentrations shows the smaller values of A_0, which is not indicating the sign of interaction between the host and guest molecules.

3.2. *Surface Potential-Area (ΔV-A) Isotherm and Effective Dipole Moment ($\mu_\perp$) Measurement of Calix[n]arene and Calix[n]arene-PABA*

The ΔV-A isotherm reveals the molecular orientation changes of the C4, C6, C4-PABA, and C6-PABA monolayer film at the air-water interface upon compression by the barriers in the Langmuir trough. Then, the $\mu_\perp$ of all Langmuir films has been determined from the results of ΔV-A isotherm using Eq. 1. The ΔV-A and $\mu_\perp$-A isotherms for 2100 μl of C4 and C6, as shown in Figure 6 reveal the orientation of molecules during compression. The progressive increase of ΔV is caused by $\mu_\perp$ during the compression due to the stretching out of the hydrophobic region of calixarenes at the air-water interface, resulting in a change in molecular orientation (Al-Alwani et al., 2022). When the monolayer changes its state from 2-D gaseous to 2-D liquid, and 2-D liquid to 2-D solid, the flexures occur in the isotherm. This happens due to the rearrangement and reorientation of molecules during the compression. Then, the maximum values of ΔV and $\mu_\perp$ is achieved, denoted by ΔV_{max} and $\mu_{\perp max}$ determined by interpolating the $\mu_{\perp max}$ towards the ΔV-A isotherm as shown in Figure 6, indicate the most vertical orientation of molecules (Azahari et al., 2014). A reorientation of the μ is indicated by the decrease of ΔV and $\mu_\perp$ upon further compression, followed by the collapsing of the monolayer (Bland et al., 2019; Chachaj-Brekiesz et al., 2021; da Silva et al., 2020). The ΔV-A and $\mu_{\perp}$-A isotherms for C4-PABA and C6-PABA shown in Figure 7 show the same behaviour as well, that the rearrangement and reorientation of molecules are indicated by the flexures.

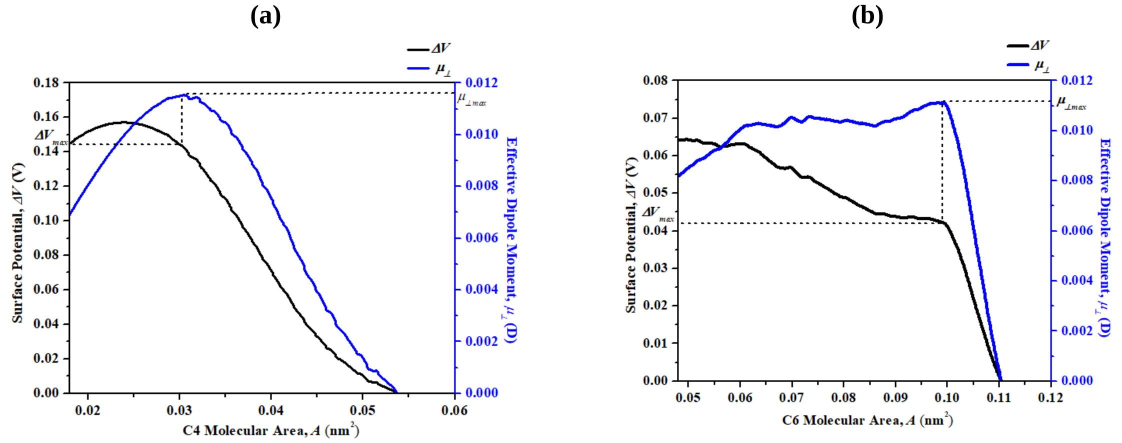

Figure 6. (a) ΔV-A and $\mu_{\perp}$-A isotherms of C4 and (b) C6

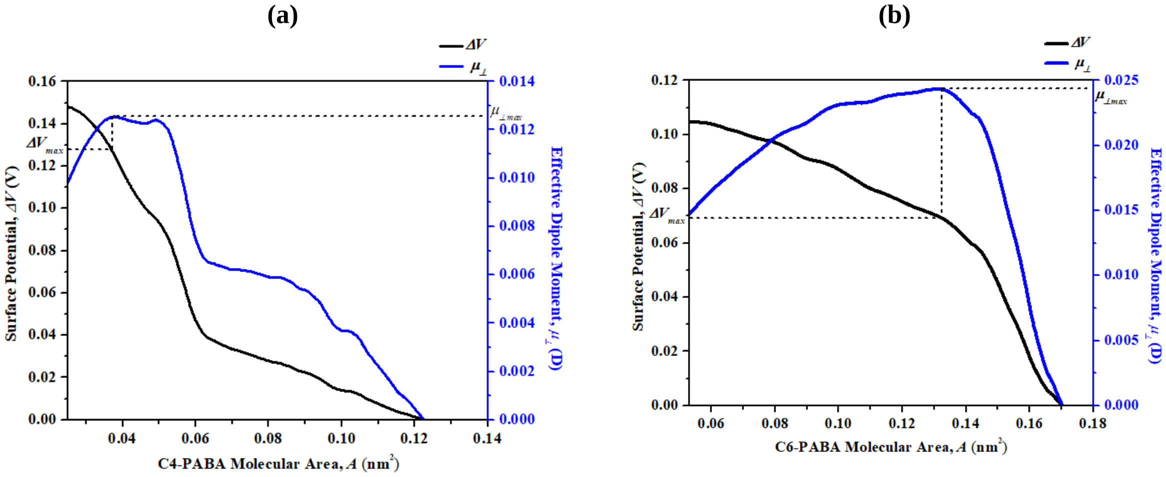

Figure 7. (a) ΔV-A and $\mu_{\perp}$-A isotherms of C4-PABA and (b) C6-PABA

Both of the maximum ΔV (ΔV_{max}) and the maximum values of $\mu_{\perp}$ ($\mu_{\perp max}$) indicate the changes in molecular structure (Azahari et al., 2014; Supian et al., 2010). The ΔV_{max} and $\mu_{\perp max}$ determined based on the ΔV-A and $\mu_{\perp}$-A isotherms presented in Table 2, Figure 8, and Figure 9 reveal the interaction between C4 and C6 with PABA molecules in the range of detectable concentrations, as discussed in the previous section.

As the PABA concentration increases, the ΔV_{max} and $\mu_{\perp max}$ show an increasing trend compared to the pure C4 and C6 monolayers. This indicates the Langmuir films become more tightly packed due to the increase in taking an upright position by molecules (Jurak et al., 2021). However, at critical concentrations, the ΔV_{max} and $\mu_{\perp max}$of C4-PABA and C6-PABA reach their maximum values. As shown by the circle marker icons in Figure 8 and Figure 9, the decreasing trends of ΔV_{max} and $\mu_{\perp max}$ are shown after those critical concentrations at the corresponding kink points, which are at the PABA concentration of 0.065 mg/ml and 0.045 mg/ml for C4-PABA and C6-PABA, respectively. These results are in good agreement with the previous research made that the monolayer is not reacting anymore with the drugs present since the decrease in $\mu_{\perp}$ is shown with the increasing drug concentration. Otherwise, the $\mu_{\perp}$ should be increased (Hidalgo et al., 2004).

Table 2. The ΔV_{max} and $\mu_{\perp max}$ of calix[n]arene-PABA Langmuir Films

C4			C6		
PABA Concentration (mg/ml)	ΔV_{max} (V)	$\mu_{\perp max}$ (D)	PABA Concentration (mg/ml)	ΔV_{max} (V)	$\mu_{\perp max}$ (D)
0	0.14243	0.01153	0	0.04276	0.01112
0.035	0.12482	0.01256	0.020	0.06965	0.02435
0.040	0.11142	0.01159	0.025	0.10097	0.03711
0.045	0.14128	0.01807	0.030	0.08339	0.02514
0.050	0.18030	0.02369	0.035	0.10238	0.03269
0.055	0.20011	0.02645	0.040	0.10473	0.03466
0.060	0.20811	0.02662	0.045	0.16478	0.04658
0.065	0.22185	0.03827	0.050	0.09803	0.03679
0.070	0.16745	0.01938	0.055	0.11003	0.03715
0.075	0.17774	0.02113	0.060	0.10966	0.03059
0.080	0.15986	0.01807			

(a) **(b)**

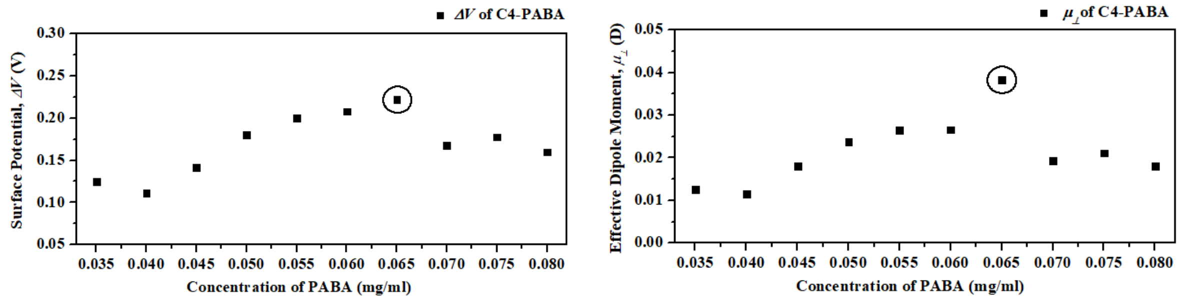

Figure 8. Graph of (a) ΔV_{max} and (b) $\mu_{\perp max}$ versus PABA concentration for C4-PABA

(a) **(b)**

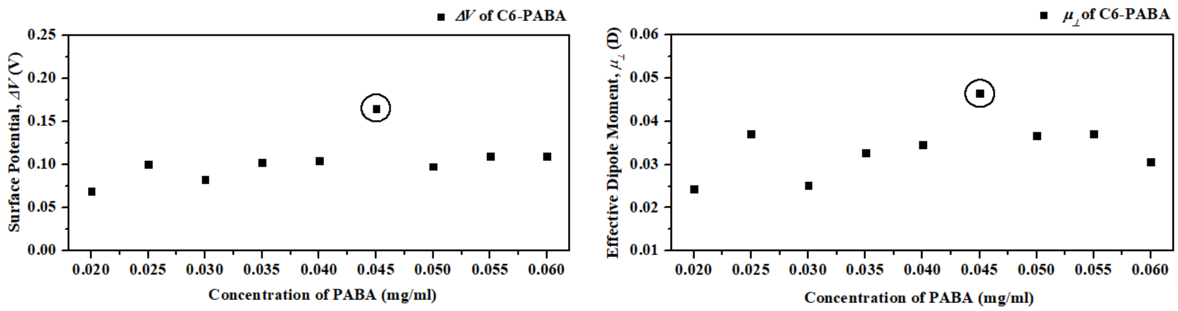

Figure 9. Graph of (a) ΔV_{max} and (b) $\mu_{\perp max}$ versus PABA concentration for C6-PABA

This indicates that the sensing of PABA with the maximum number of C4 and C6 has been achieved at the PABA concentration of 0.065 mg/mL (0.4740 mM) and 0.045 mg/mL (0.3281 mM), respectively. At the same time, the monolayers have the greatest stability at those optimum concentrations since a Langmuir film with a lower ΔV_{max} is more disordered and less stable compared to a Langmuir film with a higher ΔV_{max} (Chachaj-Brekiesz et al., 2021; Dynarowicz-Łątka et al., 2002). At those critical concentrations, the molar ratio of 1:1.006 for C4 to PABA and 1:1.045 for C6 to PABA are shown, respectively. This formation ratio is in good agreement with previous studies regarding the 1:1 host-guest complex formed by small macrocyclic calixarenes, which are C4 and C6 (Sanku et al., 2019).

3.3. Host-Guest Sensing Interactions of Calix[n]arene-PABA Complexes

Due to the amphiphilic property of calixarenes, the interactions between C4 and C6 with PABA molecules take place at the lower rims located at the air-water interface. In the host-guest interaction between calixarenes and PABA, the O atoms from the hydroxyl group owned by the calixarenes contribute to the sensing of PABA molecules. In an aqueous solution, the negative site of calixarenes at its O atoms with lone pair favours the formation of the complex by calixarenes with PABA cation via electrostatic or ion-dipole interaction. Besides, the sensing of PABA anion is extended by hydrogen bonding or dipole-dipole interaction with partial positively charged phenoxy O atoms in the structure of calixarenes. On the other hand, the neutral PABA molecule could be detected by calixarene through the formation of hydrogen bonding between PABA and phenoxy O atoms from calixarenes. These interactions are supported by the studies made by previous researchers regarding the interaction between calixarenes with ions and neutral molecules (De Leener et al., 2022; Fahmy et al., 2018; Pellegrini, 2011; Priyangga et al., 2022).

Since the intermolecular packing structures of C4, C6, C4-PABA, and C6-PABA are different, their monolayers' properties also differ according to the isotherms' results. Based on the isotherm results, the presence of PABA within the subphase is detected by both C4 and C6 with different A_0, ΔV_{max} and $\mu_{\perp max}$ of their complexes, respectively, which indicates the successful sensing of PABA by calixarenes in this study.

Based on the Π-A isotherm in this study, the collapse pressure of C4, C6, C4-PABA, and C6-PABA indicate the stability of Langmuir films. A monolayer with lower collapse pressure is less resistant to compression and less stable (da Rocha Rodrigues et al., 2020; Dynarowicz-Łątka et al., 2002). The C4 Langmuir film is more stable since the collapse pressure of C4 (61.0159 mN/m) is higher than C6 (57.3904 mN/m). At the same time, the C4-PABA Langmuir film is more stable since the collapse pressure of C4-PABA (55.2191 mN/m) is higher than C6-PABA (37.2709 mN/m). This shows that a more stable monolayer is formed by C4-PABA compared to C6-PABA.

Besides, a Langmuir film with a lower ΔV_{max} is more disordered and less stable compared to Langmuir film with higher ΔV_{max} (Chachaj-Brekiesz et al., 2021; Dynarowicz-Łątka et al., 2002). Based on the ΔV-A isotherm, the C4 Langmuir film is more stable since the ΔV_{max} for C4 (0.14243 V) is higher than C6 (0.04276 V). At the same time, the C4-PABA Langmuir film is more stable since the ΔV_{max} of C4-PABA (0.22185 V) is higher than C6-PABA (0.16478 V) at their optimum concentrations. This shows that a more stable Langmuir film is formed by C4 with PABA compared to C6.

Both the Π-A and ΔV-A isotherms show a consistent result that C4 is capable to form a more stable Langmuir film than C6. When applying the Langmuir technique in the sensing of PABA, the C4-PABA demonstrates higher stability compared to the C6-PABA monolayer. The formation of C4 followed by the C4-PABA monolayer is more stable due to the delicate spatial control performed by the small rim geometry of C4 (Troian-Gautier et al., 2020). This suggests the superiority of C4 in the sensing of PABA compared to C6 using the Langmuir technique.

4. CONCLUSION

The mechanism of host-guest interaction between two types of calixarenes, which are C4 and C6, with PABA as host and guest molecules, respectively have been studied based on the Π-A, ΔV-A isotherms. Based on the results of Π-A isotherm, the formation of C4 and C6 monolayers using 2100 μl is considered stable. The detectable concentration ranges of PABA for C4 and C6 are from 0.035 mg/ml to 0.080 mg/ml, and from 0.020 mg/ml to 0.060 mg/mL respectively. Besides, the kink points observed based on the values of A_0, ΔV_{max} and $\mu_{\perp max}$ of calixarene-PABA complexes calculated to show that the interaction between C4 and C6 with PABA exists at the molar ratio of 1:1 for each complex. The superiority of C4 in the sensing of PABA compared to C6 using the Langmuir technique is suggested. Results obtained in this study may be applied to drug sensor applications in the field of medicine and pharmaceutical.

However, the properties of calixarene-PABA complexes should be studied and considered before being used in any application. Further studies, the host-guest mechanism of other calixarenes families with different types of materials or compounds can be explored for more potential applications.

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