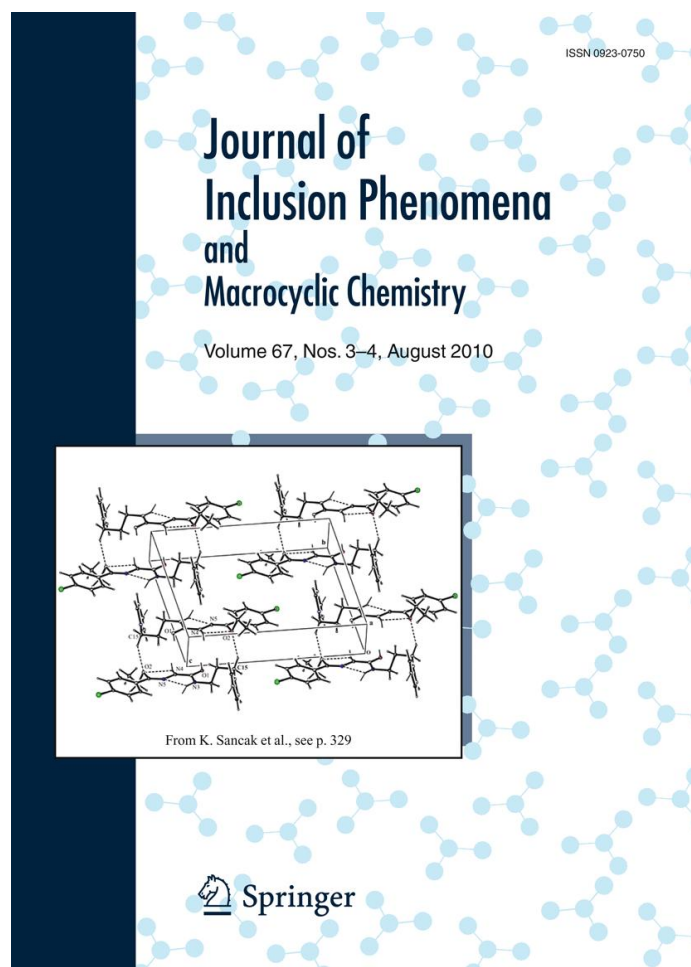


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Thermodynamic study of functionalized calix[n]arene and resorcinol[n]arene monolayers spreaded at an aqueous pendant drop

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Abstract The behavior of insoluble calix[n]arene and resorcinol[n]arene derivatives monolayers were studied through the use of a constant surface Langmuir balance based on Axisymmetric Drop Shape Analysis (ADSA). In each case, a stable monolayer was obtained and different transitions (induced for lateral compression) could be identified. Thermodynamic parameters were computed through two dimensional Clausius–Clayperon equations and used to valuate the monolayer stability. A noticeable reduction of thermodynamic parameters occurred at highly tested temperatures (328 and 338 K) for those compounds that had hydrocarbon tails or benzene rings attached to one side of macrocyclic rim. Such fact was related to a monolayer rearrangement where the macrocyclic ring changed from a parallel to a perpendicular orientation. In

this orientation the hydrophobic interactions between hydrocarbon chains and benzene rings were maximized. At highly temperature, where vigorous molecular motion existed, those interactions were superior to the stabilization effect through hydrogen bond.

Keywords Langmuir monolayers · Calix[n]arenes · Resorcinol[n]arenes · ADSA · Conformational changes · Thermodynamic

Introduction

Calixarenes are versatile macrocyclic compounds that present a hydrophobic core sandwiched between two functionalizable rims [1, 2]. As a result, these compounds are insoluble in water, but their dissymmetrical polar structure allows them self-assembly into Langmuir monolayers [3].

The possibility of an easy chemical modification has allowed them to serve as molecular platforms for the constructions of gases, both cations and anions, small organic or biological interest molecule receptors [4], and the formation of nano-capsules [5–8]. These structures use hydrogen bonding or metal coordination to ensure their structural integrity. The perspective of obtaining self-assembled structures with such compounds (that potentially can act as receptors) has driven the authors to explore the possibility of obtaining self-assembly molecular aggregates from calix[n]arenes [9–11]. From biomedical point of view the para-acyl calix[n]arenes present new transport properties which combined with a lack of toxicity makes them useful candidates for drug vectorization [4].

The aim of this paper is to obtain precise information from the behavior of Langmuir monolayers of three

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functionalized calix[n]arenes and two resorcinol[n]arenes derivatives spread over a water subphase by the employ of a constant surface pressure penetration Langmuir balance based on the Axisymmetric Drop Shape Analysis (ADSA). The drop shape analysis appears to be a useful technique enabling study of the adsorption phenomena at liquid/liquid and liquid/air interfaces. Among the interfacial tension techniques, ADSA [12, 13] is one of the most precise and versatile. It fits experimental drop profiles (obtained from digital drop micrographs) to the Laplace equation of capillarity, and provides the interfacial tension γ and area A as outputs. It is noninvasive; i.e. the measuring device is not in direct contact with solvent or the adsorbate and does not interact with them.

For all derivatives, we recorded the surface pressure and the corresponding molecular area of the monomolecular film spread over an air/water interface at different temperatures. We obtained for each monolayer: the limiting area, the compressibility modulus and the collapse pressure values. Our attention was focused on the effect of temperature on molecular phase transitions. Thermodynamic parameters were computed and were evaluated as an indicator of the system stability. The experiments were performed as a previous step in the future use of the tested molecules in more complex supramolecular assemblies with the aim of developing chemical sensitive systems designated as ion channel sensors. The information obtained will be useful in selecting suitable materials and can lead to a decrease of the trials and errors steps involved [14–16].

Experimental

Materials

p-tert-butylcalix[4]arene (CALIX4, ref. 423246), *p*-tert-butylcalix[6]arene (CALIX6, ref. 434108), *p*-tert-butylcalix[8]arene (CALIX8, ref. 69066) were from Sigma–Aldrich Chemical Co. *p*-tert-butylcalix[4]arene-*O*-butyl acetate (CALIX4OBA), *p*-tert-butylcalix[6]arene-*O*-butyl acetate (CALIX6OBA), *p*-tert-butylcalix[8]arene-*O*-butyl acetate (CALIX8OBA), *p*-tolyl-[4]resorcinarene (RESOR4) and *p*-tolyl-[4]-resorcinarene-*O*-diethyl diacetate (RESOR4ODEDA) have been synthesized as already described Pieroni et al. [17–22]. Before used, all compounds were recrystallized three times from ethanol-ethyl acetate (5:1) and purified by column chromatography on silica gel using benzene-ethyl acetate (4:1) as eluent. The purity of all samples was judged to be >99%, as evidenced by the combination of ^1H ; ^{13}C NMR; mixed Mp (melting point) and thin layer co-chromatography techniques [17–22].

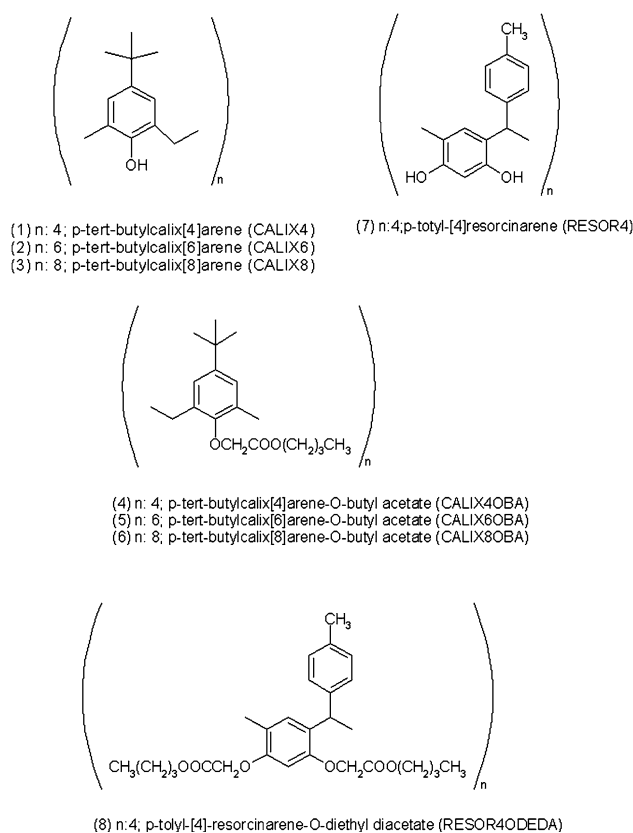


Fig. 1 Calix[n]arene and resorcinol[n]arene molecular structures

p-tolyl-[4]resorcinarene (RESOR4) and *p*-tolyl-[4]-resorcinarene-*O*-diethyl diacetate (RESOR4ODEDA) correspond to the isomer in configuration *cis*–*cis*–*cis* (*rccc*, “*r*” refers to the resorcinol residue) and *cis*–*trans*–*trans* (*rctt*) respectively. Structures of compound were tested by NMR. The NMR spectra indicated that the *rccc* isomer exists as cone conformation and the *rctt* isomer as chair conformation [22]. For a reference their structures are shown in Fig. 1.

Apparatus and operation condition

The experiments were performed with a constant surface pressure penetration Langmuir balance based on Axisymmetric Drop Shape Analysis (ADSA) [12, 13]. The whole setup, including the image capturing, the micro-injector, the ADSA algorithm, and the fuzzy pressure control, is managed by a Windows integrated program (DINATEN). A solution droplet is formed at the tip of a capillary, which is outer one of an arrangement of two coaxial capillaries connected to the different branches of a micro-injector. These can operate independently, permitting one to vary the interfacial area by changing the drop volume, and to exchange the drop content by through flow. The software

first detects the drop and with an appropriate calibration, transforms it into physical coordinates. Then the experimental drop profiles, extracted from digital drops micrographs, are fitted to the Young–Laplace equation of capillarity by using ADSA. This process is performed automatically, the liquid density difference and the local gravity being the only inputs and yielding as outputs the drop volume V , the interfacial tension γ and the surface area A in about 0.3–5 s for each picture, depending on the required precision. Area control uses a modulated fuzzy logic PID (proportional, integral and derivative control) algorithm and is controlled by changing the drop volume. During the experiment, the drop is immersed in a thermostated and vapor-saturated standard spectrophotometer cuvette (Hellma®) minimizing contamination and drop evaporation. The surface pressure is obtained from the relationship $\pi = \gamma_0 - \gamma$, where π is the surface pressure; γ and γ_0 are the surface tension of the subphase liquid covered with and without the monolayer. The setup is placed on a pneumatic vibration-damped optical bench table in a clean laboratory. All experiments were performed at (25.0 ± 0.1) °C. Temperature was maintained by a thermostat bath with recycling water throughout all the experiment. The curves were highly reproducible: each experiment was done three times, the standard deviation [23] on π and A was estimated to be ± 0.01 mJ m⁻² and ± 0.005 nm² molec⁻¹, respectively. Equation fitting were done from non-linear procedures using ORIGIN® computer package (release 7.0).

Monolayers

Spreading solutions of each compound were prepared dissolving the properly quantity in a methanol: chloroform mixture (1:4) to obtain solutions of (2.08×10^{-5}) M total concentration. Then an aliquot of 1 μ L (for compounds 1, 3, 4, 6, 7 and 8), 1.2 μ L (for compound 2) and 1.8 μ L (for compound 5) was spread on the water drop using a micro syringe following Li et al. procedure [24]. Four minutes were allowed for solvent evaporation before starting the expansion until a volume of 25 μ L. The compression rate was 0.25 μ L s⁻¹ (0.18 cm² min⁻¹). For such value the best curves reproducibility was attained. When expansion was finished the program maintain the drop area constant for 118 s to reach the monolayer equilibrium, then the compression starts at the same rate of expansion process.

Theoretical section

The entropy change (ΔS) and the latent heat (ΔH) of surface transitions can be determined through Clausius–Clayperon equation in two dimensions [25]:

$$\left(\frac{d\pi}{dT}\right) = \frac{\Delta\bar{S}_{\alpha\rightarrow\beta}}{\Delta\bar{A}_{\alpha\rightarrow\beta}} \quad (1)$$

where $\Delta S_{\alpha\rightarrow\beta}$ and $\Delta A_{\alpha\rightarrow\beta}$ are the changes in molar entropy and molar area, respectively, that accompany the phase transition from α to β . An alternate form of this equation in which the temperature dependence of the surface pressure, π , appears rather than that of the surface tension, γ , has been employed in the literature [26]. As correctly reported by several authors [27, 28], the extraction of thermodynamic parameters requires the removal of the water temperature surface tension dependence, γ_0 , according to:

$$\left(\frac{d\gamma}{dT}\right) - \left(\frac{d\gamma_0}{dT}\right) = \frac{\Delta\bar{S}_{\alpha\rightarrow\beta}}{\Delta A_{\alpha\rightarrow\beta}} \quad (2)$$

$$\Delta H = \Delta ST = (d\pi_T/dT) \Delta AT \quad (3)$$

For all tested molecules, the equilibrium surface pressure (taken at the midpoint between the two slope changes which delimited a transition) is plotted as a function of temperature in Fig. 2. We found that the surface pressure transition decreases with increasing temperature (see Fig. 2) but not in a linear fashion. A linear regression implies that ΔH does not change with the temperature, which is often not the case. Taking into account the curvature of the obtained plots, $(d\pi/dT)$ values were found from derivation of individual regression functions. Obtained results were summarized in Tables 1 and 2.

The appropriate enthalpy includes the surface work term according to

$$\Delta H = \Delta E + \Delta(PV) + \Delta(\gamma A) \quad (4)$$

At constant pressure, volume and surface tension we have:

$$\Delta H = \Delta E + \gamma \Delta A \quad (5)$$

where ΔA is the area change per molecule at the phase transition. In this study, we used the width of the plateau in each π vs. A isotherm as ΔA value. A meaningful value of $(d\pi/dT)$ could be obtained for samples which exhibited constant pressure transitions plateaus at several temperatures. The magnitude of the change in area that accompanies the transition, $|\Delta A|$, clearly decreased with temperature augment.

Results and discussion

The π vs. A isotherms of the studied compounds are shown in Figs. 3, 4, 5, 6, 7, 8. For all tested calix[n]arenes derivatives, the obtained curves showed inflexion zones (slope changes) and plateau regions. Plateau regions are

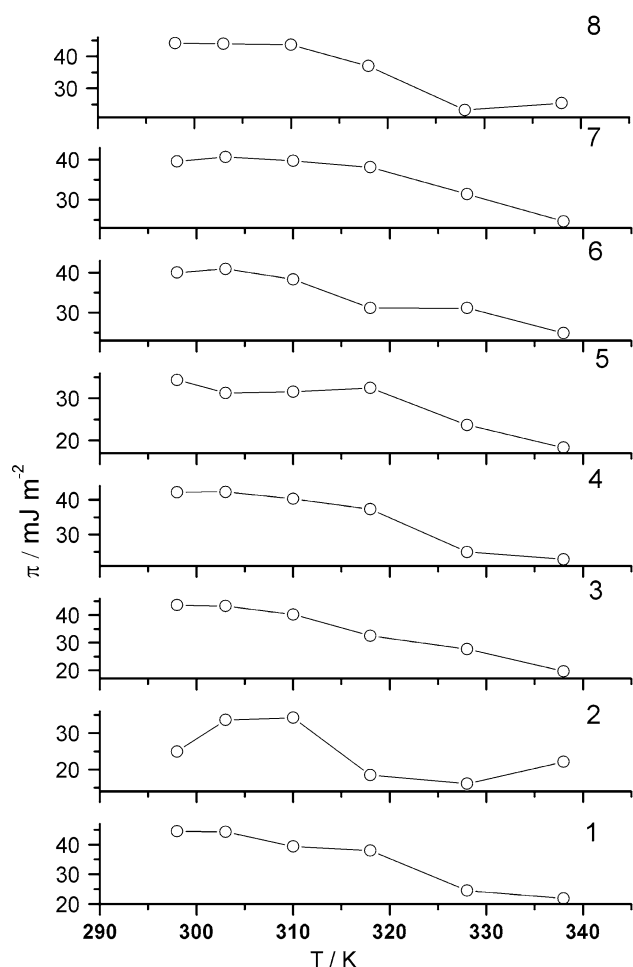


Fig. 2 Equilibrium surface pressure (π , taken at the midpoint between the two changes in slope delimiting the transition) plotted as a function of temperature (T) for: (1) CALIX4; (2) CALIX6; (3) CALIX8; (4) CALIX4OBA; (5) CALIX6OBA; (6) CALIX8OBA; (7) RESOR4; (8) RESOR4ODEDA

usually ascribed to zones of phase coexistence (both phases coexist in equilibrium) [29]. This fact usually occurs when the monolayer is less compressible. Sometimes the coexistence of phases can not be assessed, and only is seen a slope change in the isotherm which corresponds to a phase transition [30]. For the specific case of calix[n]arenes derivatives, the changes in the isotherm profiles could not be attributed to a phase transition phenomena because the behavior of the surface pressure as a function of time is the typical for a stable Liquid Expanded (LE) film. However, these changes are assumed due to changes in orientation of the calix[n]arene macrocyclic rings [31, 32] forced by the pendant drop lateral compression. In some cases more than one transition was noted. The identified changes depended on surface pressure, temperature and the molecular structure.

Calix[8]arene derivatives

Calix[8]arenes derivatives, which have a large cavity, are mobile and flexible in solution [33]. The dimension of their ring allows an appreciable conformational freedom [34]. Whatever their mobility, it is very probable that they adjust themselves at the interface adopting a conformation that maximizes their attractive interactions.

The inspection of π vs. A isotherm obtained for native *p*-*tert*-butyl calix[8]arene at 298 K (Fig. 3) showed two changes in the curve profile: (i) one that occurred at $A \approx 2.50 \text{ nm}^2 \text{ molec}^{-1}$ and (ii) a final plateau transition which begun at $A = 2.00 \text{ nm}^2 \text{ molec}^{-1}$. At light of the obtained results, we supposed that at low compression ($A > 3.22 \text{ nm}^2 \text{ molec}^{-1}$) this molecule presented a pleated loop conformation [35]. As surface pressure augmented the pleated loop conformation was replaced by a cone/cone conformation (syn and anti). The molecular area or calix[8]arene in a syn or anti cone/cone conformations calculated by Corey–Pauling–Koltum (CPK) molecular models was $2.73 \text{ nm}^2 \text{ molec}^{-1}$ and $2.44 \text{ nm}^2 \text{ molec}^{-1}$ [36] respectively. This fact would explain the isotherm slope change at $A = 2.50 \text{ nm}^2 \text{ molec}^{-1}$. Further compression caused a new conformational change (the beginning of plateau region) which in agreement with CPK models would be due to a 1,3,5,7-alternate conformation. So far, the macrocyclic ring all the time would be parallel to subphase, such a disposition would encourage the formation of hydrogen bonds with water molecules. In the alternate conformation, the alternate $-\text{OH}$ groups also favored the formation of intermolecular H-bonds between calix molecules resulting in a monolayer additional stabilization.

During the final transition there was a drastic molecular area reduction (from 2.00 to $1.25 \text{ nm}^2 \text{ molec}^{-1}$). Such fact would be supposed to be due to the change of macrocyclic ring orientation from a parallel to a perpendicular orientation [36]. The existence of a plateau region in the isotherm indicated that both conformations coexist simultaneously. Similar results were observed from the inspection of isotherms collected at 303 to 328 K. Temperature had no significant effect over the molecular area or transitions but reduced notably the values of surface pressures (this fact was more evident at maximum compression). This fact implied a reduction of the molecular units anchorage at the interface. So, a decrease of monolayer stability (which was evidenced by the augment of thermodynamic parameters, see Table 1) occurred. The same effect caused the disappearance of plateau region at 338 K.

Temperature effect was significant for the CALIX8OBA isotherm, Fig. 4. This is assumed to be due the presence of it bulkier groups at both rims and it less flexible structure.

Table 1 Thermodynamic parameters computed (Eqs. 2, 3 and 5) for limited ^(lim) and intermediated ⁽¹⁾ transitions of the tested calix[n]arenes derivatives at different temperatures

T/K	⁽¹⁾ ΔS J/K mol	⁽¹⁾ ΔH kJ/mol	⁽¹⁾ ΔE kJ/mol	^(lim) ΔS J/K mol	^(lim) ΔH kJ/mol	^(lim) ΔE kJ/mol
CALIX4						
298	60.41 ± 1.20	18.00 ± 0.62	28.19 ± 1.12	-14.66 ± 0.65	-4.37 ± 0.30	-7.49 ± 0.60
303	68.46 ± 1.34	20.74 ± 0.57	33.12 ± 0.99	15.62 ± 0.73	4.73 ± 0.33	2.67 ± 0.60
310	77.86 ± 0.80	24.14 ± 0.98	39.42 ± 1.04	47.07 ± 0.24	14.59 ± 1.23	8.90 ± 1.01
318	84.57 ± 0.96	26.89 ± 1.04	44.04 ± 2.36	50.52 ± 1.34	16.07 ± 0.96	13.13 ± 0.98
CALIX8						
298				-9.39 ± 1.02	-2.79 ± 0.62	-6.31 ± 0.78
303				38.71 ± 2.45	11.73 ± 2.36	-0.02 ± 0.60
310				125.78 ± 3.56	38.99 ± 2.45	21.91 ± 0.89
318				246.59 ± 5.98	78.41 ± 2.65	60.71 ± 1.09
328				291.06 ± 6.02	95.47 ± 3.97	68.31 ± 1.10
338				388.89 ± 6.08	131.44 ± 4.35	99.44 ± 1.20
CALIX4OBA						
298				-88.99 ± 3.20	-26.52 ± 1.97	-41.99 ± 3.15
303				-5.28 ± 1.02	-1.60 ± 0.73	-8.90 ± 1.28
310				56.05 ± 2.51	17.37 ± 1.07	6.60 ± 0.76
318				104.10 ± 2.65	33.10 ± 1.25	27.33 ± 1.22
328				63.33 ± 2.42	20.77 ± 1.32	-3.98 ± 0.93
338				6.64 ± 1.17	2.24 ± 0.73	-4.96 ± 0.91
CALIX80BA						
298				-139.18 ± 2.21	-41.47 ± 0.92	-54.90 ± 1.13
303				-22.07 ± 0.86	-6.68 ± 0.66	-18.02 ± 0.65
310				165.32 ± 1.98	51.25 ± 1.09	39.19 ± 1.33
318				211.24 ± 1.77	67.17 ± 1.08	36.58 ± 1.40
328				154.01 ± 1.63	50.52 ± 1.10	45.25 ± 0.92
338				41.48 ± 0.92	14.01 ± 0.93	9.68 ± 0.77

Table 2 Thermodynamic parameters computed (Eqs. 2, 3 and 5) for limited ^(lim) and intermediated ⁽¹⁾ transitions of the tested resorcinol[n]arenes derivatives at different temperatures

T/K	⁽¹⁾ ΔS J/K mol	⁽¹⁾ ΔH kJ/mol	⁽¹⁾ ΔE kJ/mol	^(lim) ΔS J/K mol	^(lim) ΔH kJ/mol	^(lim) ΔE kJ/mol
RESOR4						
298	88.13 ± 5.89	26.26 ± 1.26	38.00 ± 1.32	-108.55 ± 5.13	-32.35 ± 0.76	-41.55 ± 2.34
303	67.93 ± 3.20	20.58 ± 1.08	29.58 ± 1.21	-63.81 ± 2.44	-19.33 ± 0.82	-29.38 ± 2.03
310	93.64 ± 4.72	29.03 ± 1.09	42.59 ± 1.05	2.43 ± 0.98	0.75 ± 0.50	-7.61 ± 0.97
318	82.62 ± 2.87	26.27 ± 1.11	37.76 ± 1.24	42.96 ± 2.33	13.66 ± 1.01	8.24 ± 0.86
328	93.64 ± 1.99	30.71 ± 1.07	48.10 ± 1.33	96.67 ± 3.64	31.70 ± 1.28	23.98 ± 1.10
338	124.85 ± 2.21	42.20 ± 1.15	65.62 ± 1.28	31.42 ± 2.43	10.62 ± 0.99	7.72 ± 0.98
RESOR4ODEDA						
298				-59.33 ± 3.33	-17.68 ± 1.07	-30.98 ± 1.04
303				-78.03 ± 2.87	-23.64 ± 1.23	-42.23 ± 1.15
310				13.44 ± 1.99	4.17 ± 0.87	2.76 ± 0.94
318				67.96 ± 2.08	21.61 ± 1.30	19.02 ± 1.02

For the experiments carried out from 298 to 328 K, the compression caused the same effect observed for the CALIX8 monolayers. At higher temperatures (328 and

338 K) there was a loss of plateau regions and a diminution of thermodynamic parameters. At such conditions the adopted conformation favored strong intermolecular

Fig. 3 π -A isotherms of *p*-*tert*-butylcalix[8]arene spreaded on water subphase at 298 K: **a** Plated loop: these flatter conformation do not have the cone-shape cavity [35]; **b** syn cone/cone conformation; **c** anti cone cone conformation; **d** parallel and perpendicular interface orientation phase coexistence region. Insert: π -A isotherms of *p*-*tert*-butylcalix[8]arene spreaded on water subphase at: (1) 298 K; (2) 303 K; (3) 310 K; (4) 318 K; (5) 328 K and (6) 338 K

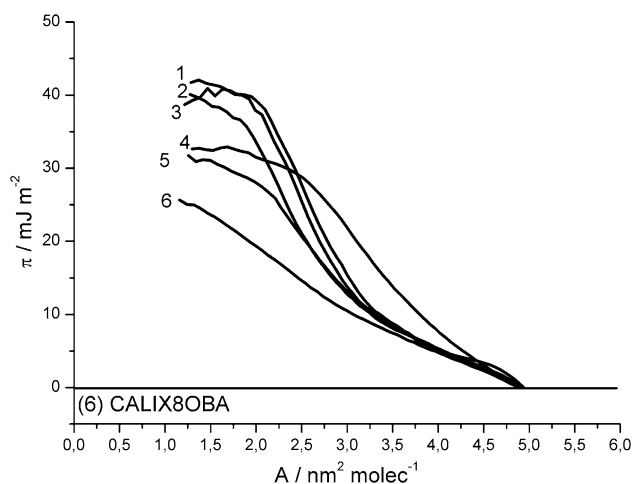
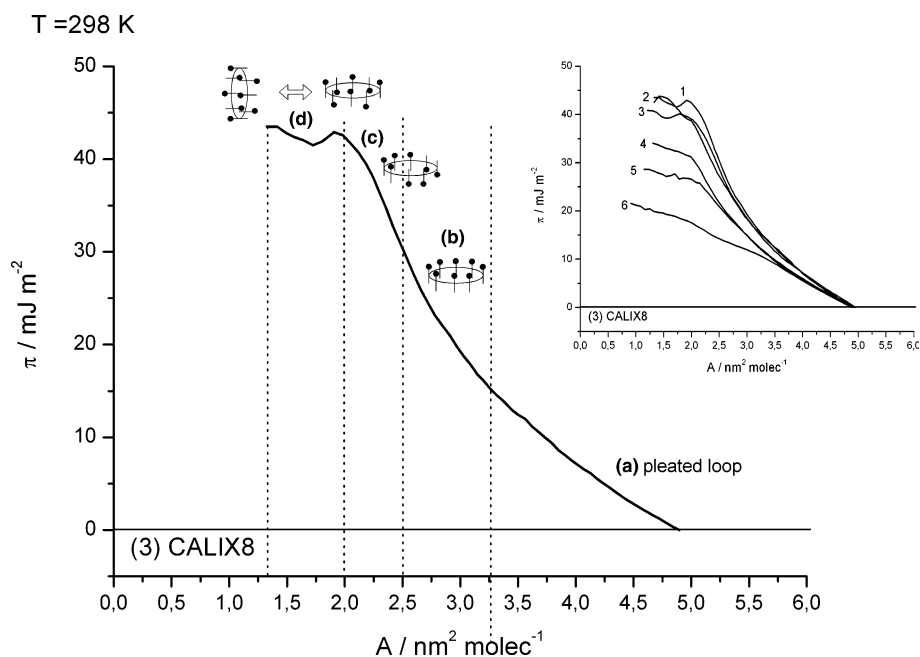


Fig. 4 π -A isotherms of *p*-*tert*-butylcalix[8]arene-*O*-butyl acetate spreaded on water subphase at: (1) 298 K; (2) 303 K; (3) 310 K; (4) 318 K; (5) 328 K and (6) 338 K

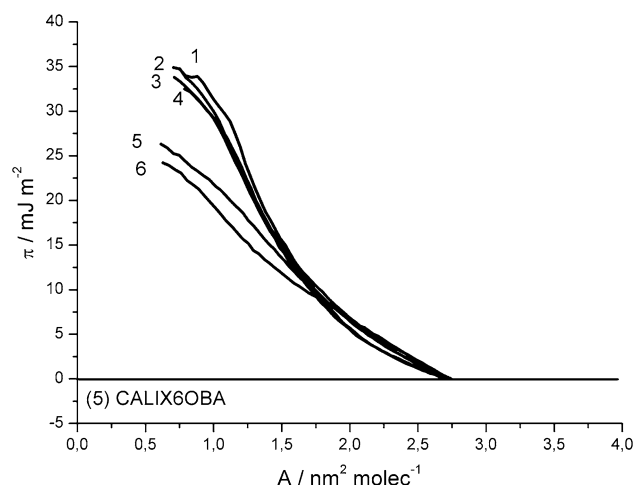


Fig. 5 π -A isotherms of *p*-*tert*-butylcalix[6]arene-*O*-butyl acetate spreaded on water subphase at: (1) 298 K; (2) 303 K; (3) 310 K; (4) 318 K; (5) 328 K and (6) 338 K

hydrophobic interactions between alkyl chains counteracting the energetic contribution due to Brownian motions which caused the monolayer destabilization.

Calix[6]arene derivatives

CALIX6 and CALIX6OBA are macrocyclic hexamers that have a great tendency to lie at the air–water interface at 298 K in a hexagonally packed array [37]. From inspection of π vs A . plots (Fig. 5) we assumed that at low surface pressures, both compound adopted a pinched cone (winged) conformations [35] ($A > 3.20 \text{ nm}^2 \text{ molec}^{-1}$). With the increment of surface pressure or temperature, the

CALIX6 isotherm showed a slope change at $A = 1.78 \text{ nm}^2 \text{ molec}^{-1}$ which could be related to pinched cone \rightarrow cone with alternate conformation transition. At all temperatures, further compression provoked a final change of the calix ring from a parallel to a perpendicular orientation to water surface ($A = 1.07 \text{ nm}^2 \text{ molec}^{-1}$).

Temperature effect was more evident in CALIX 6 than in CALIX6OBA isotherms. A molecular area reduction for CALIX6OBA monolayer was also appreciated. The intermolecular hydrogen bonding between phenolic $-\text{OH}$ groups belonging to adjacent molecules (favored due to the alternate conformation adopted) and the hydrophobic interactions that occurred between alkyl chains were the

Fig. 6 π - A isotherms of *p*-*tert*-butylcalix[4]arene spreaded on water subphase at 298 K: (a) cone conformation; (b) cone and partial cone conformation phase coexistence zone; (c) partial cone conformation; (d) parallel and perpendicular interface orientation phase coexistence region. Insert: π - A isotherms of *p*-*tert*-butylcalix[4]arene spreaded on water subphase at: (1) 298 K; (2) 303 K; (3) 310 K; (4) 318 K; (5) 328 K and (6) 338 K

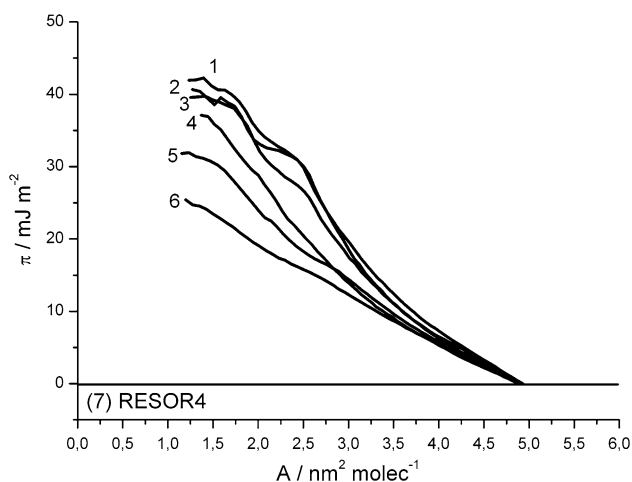
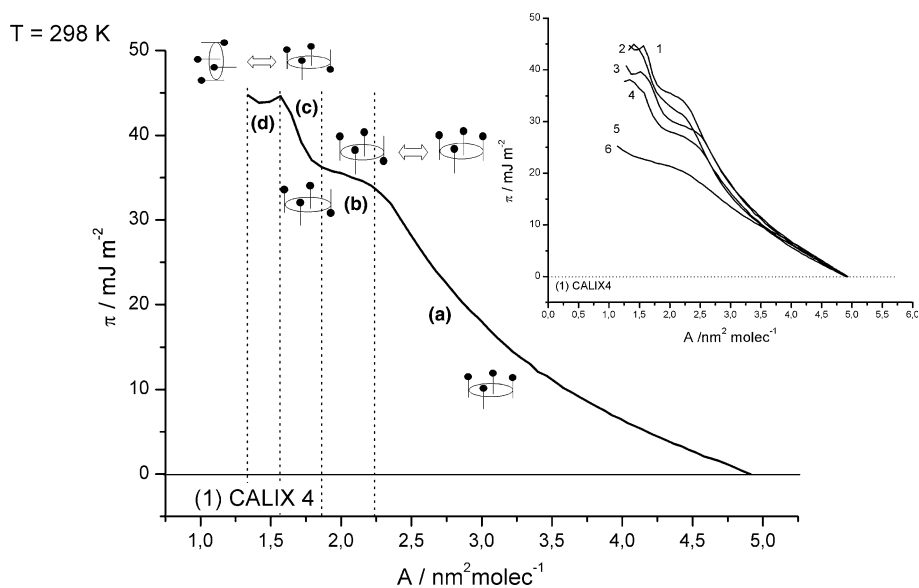


Fig. 7 π - A isotherms of *p*-tolyl-[4]resorcinarene spreaded on water subphase at: (1) 298 K; (2) 303 K; (3) 310 K; (4) 318 K; (5) 328 K and (6) 338 K

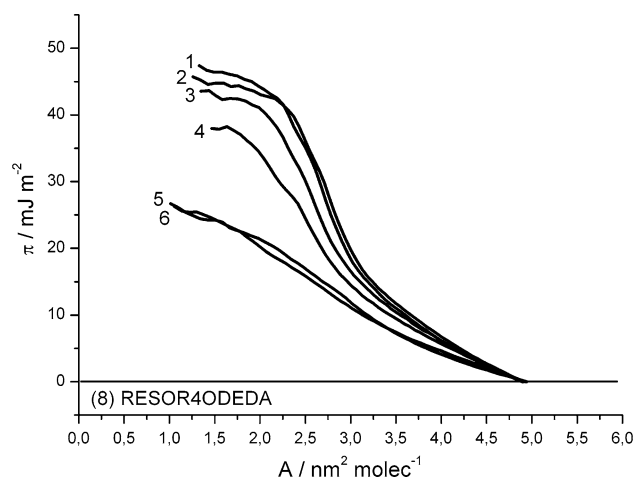


Fig. 8 π - A isotherms of *p*-tolyl-[4]resorcinarene-*O*-diethyl diacetate spreaded on water subphase at: (1) 298 K; (2) 303 K; (3) 310 K; (4) 318 K; (5) 328 K and (6) 338 K

stabilizing factors of the perpendicular orientation at high surface pressures. Transitions and limited areas obtained for such compounds agreed with the CPK models [3, 38, 39].

The isotherms of both compounds did not show evidences of plateau regions; so, the thermodynamic analysis of interfacial transitions was impossible.

Calix[4]arene derivatives

Basically, calix[4]arenes can exist in four different conformations: cone; partial cone; 1,2 alternate and 1,3 alternate. At low surface pressure it was supposed that the molecules adopted a cone conformation with calixarene ring parallel to interface. In such orientation there was a

large stabilizing effect due to hydrogen-bonding interactions between -OH groups and subphase water molecules. With compression, two different plateau regions were observed in the CALIX4 isotherms (Fig. 6) at 298–318 K: (i) one that occurred at $A = 2.55 \text{ nm}^2 \text{ molec}^{-1}$ and (ii) other that appeared at $A = 1.72 \text{ nm}^2 \text{ molec}^{-1}$. The computed thermodynamic parameters for the first transition were all positive and almost constant with T . The obtained ΔE values were consistent with the energetic barrier for the cone to partial cone transition [40]. The obtained molecular areas also agreed with CPK models. A new increment of surface pressure caused a monolayer rearrange; the second plateau region corresponded (as happened with CALIX6 and CALIX8 derivatives) to a change of macrocyclic ring orientation. The obtained ΔE , ΔS and ΔH values for such

transition augmented with the increment of T ; also a decrease of surface pressure was detected. Both facts indicated the monolayer destabilization. Stabilization effect through hydrogen bond became less important because of a vigorous molecular motion and it was assumed that the isomer acquired the partial cone conformations which change from parallel to perpendicular orientation at maximum compression. In the partial cone isomer conformation, one phenol unit was inversed and acquired a flexible seesaw motion around the inversed calixarene unit. Probably this motional freedom was more important than stabilization by H-bond. Further temperature increase (328 and 338 K) provoked a disappearance of plateau regions.

The π vs. A plot for the CALIX4OBA monolayer at (298–328) K temperature range presented an inflexion point at $2.75 \text{ nm}^2 \text{ molec}^{-1}$ and a plateau region that begun at a $2.00\text{--}1.75 \text{ nm}^2 \text{ molec}^{-1}$. The first change would be due to a cone to partial cone transition and the second due to a coexistence zone with molecules in a partial cone conformation with parallel and perpendicular orientation to the interface. Thermodynamic values computed for the final transition showed an augment until 318 K, a further temperature increase caused a diminution of ΔE , ΔS and ΔH values, such fact denoted the importance of hydrophobic interactions in the monolayer stabilization.

Calix[4]resorcinolarene derivatives

Calix[4]resorcinolarenes derivatives (compounds 7 and 8) had a crown like shape with macrocyclic ring parallel to subphase at low surface pressure. The stability of such monolayer molecules was provided by H-bond between –OH and carbonile groups. Two clearly transitions can be appreciated for compound 7, Fig. 7. From 298 to 310 K such transitions occurred at $2.70 \text{ nm}^2 \text{ molec}^{-1}$ and $1.90 \text{ nm}^2 \text{ molec}^{-1}$, respectively. Similarly to those happened with CALIX4 these transitions were supposed to be related to a conformational rearrangement into the monolayer. RESOR4 (rccc isomer) may adopted a cone and boat conformations which interconvert rapidly. At $T \geq 318 \text{ K}$ transitions occurred at high molecular areas values due to the increase of kinetic energy. In such conditions, there was a highly reduction of A_{lim} (about $1.30 \text{ nm}^2 \text{ molec}^{-1}$). This fact it was supposed to be due to the change of macrocyclic from a parallel to a perpendicular orientation which was followed by a rearrangement of the monolayer. Both facts caused a diminution of ΔS , ΔH , ΔE values. For compound 8 intermediate transitions were not distinguished, Fig. 8. RESOR4ODEDA (rctt isomer) adopted a rigid chair conformation with axial substitutes, which did not easily convert into another conformer. Due to the presence of

large hydrocarbon substitutive chains attached in one of the macrocyclic rims compound 8 was forced to adopt a chair conformation which is more rigid than cone–boat conformations of compound 7. Such fact was in agreement with the observed transitions at the π vs. A curve for compounds 7 and 8. Nevertheless A_{lim} obtained for both compound were similar, those would be possible to a final transition of macrocyclic ring from parallel to a perpendicular orientation independently of the isomer conformation.

Limited transition thermodynamic parameters computed at 298 K for CALIX4, CALIX4OBA, RESOR4 and RESOR4ODEDA noticed that the presence of alkyl chains and their subsequently hydrophobic interactions were determinative in monolayer stabilization over H-bond effect. So, highly negative values of ΔS , ΔH , ΔE were obtained for CALIX4OBA, RESOR4 and RESOR4ODEDA compared with CALIX4 (without alkyl chains). Also for CALIX4OBA, RESOR4 and RESOR4ODEDA the presence of alkyl and aryl chains stabilized the monolayer at higher temperatures.

Conclusions

The pendant drop technique offers a simple and sensible method to detect conformational changes at calix[n]arenes monolayers spreaded on air–water interface. In some cases more than one transition were noted. The identified transitions depended on temperature and that was reflected on the computed thermodynamic parameters. For those compounds that had hydrocarbon tails or benzene rings attached to one side of macrocyclic rim a noticeable reduction of thermodynamic parameters (stabilization effect) occurred at highly tested temperatures (328 and 338 K).

Comparing the macrocyclic ring substitution effect on thermodynamic parameters, for example in: CALIX4; CALIX4OBA; RESOR4 and RESOR4ODEDA which are all tetramers, we noticed that at low temperatures (298 K) and maximum compression the benzene ring presence caused the existence of high ordered and stable monolayer and that situation resisted the temperature augment (until 318 K). Nevertheless, at $T > 318 \text{ K}$, the presence of flexible hydrocarbon chains, which could intercalate easily between macrocyclic ring favoring hydrophobic interactions, overcome the effect of benzene ring.

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