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Monolayers of Chiral Calix[4]Resorcinarenes: Surface Pressure and Surface Potential Studies

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Chiral amphiphilic C-undecylcalix[4]resorcinarenes substituted with phenylethyl group or L(–)norephedrine were found to form well-organized monolayers at the aqueous solution – air interface. The substituents, L(–)norephedrine and phenylethyl group, determined the area occupied by the molecule on the water subphase. Introduction of these substituents lead also to perpendicular dipole moments of the molecules in the monolayers ca. 6 times larger than those of the parent amphiphilic calixresorcinarene, CAL11. Interactions of the compounds with K^+ were detected by the increase of the surface potential values measured at maximum packing of the monolayer. Addition of amino acids to the subphase lead to conformational changes in the monolayers evidenced by increased surface mean molecular area of the unmodified C-undecylcalix[4]resorcinarene. These changes were explained by the formation of hydrogen bonds with the amino acids at the expense of hydrogen bonding between the calixarene molecules in the monolayer. In contrast to unsubstituted calixresorcinarenes, interactions of the L(–)norephedrine- and phenylethyl-substituted molecules with amino acids could be easily recognized by the decrease of surface potential and dipole moment in monolayers formed by these calixarenes on subphases containing amino acids. A significant drop in the surface potential and an increased area per molecule demonstrated more specific interactions with selected amino acids: L(–)norephedrine-substituted calixarene interacted with D-valine and the phenylethyl-substituted, with D-tryptophan.

Keywords: Monolayers, calix[4]resorcinarenes, surface potential, surface pressure, Langmuir monolayer

INTRODUCTION

Molecular recognition of ions and neutral molecules is one of the mainstream topics in supramolecular chemistry. It is executed by macrocyclic and acyclic molecular receptors of diverse molecular architecture.

Chiral macrocyclic molecular receptors have been the subject of investigation for many years. There were many types of chiral molecular architectures, such as crown ethers, cryptands, podands, cyclophanes, cyclodextrins, or their chemical modifications. The goal was to use them as a means for recognition of enantiomeric species by the process of molecular recognition. It should be noted, however, that practically all the above-mentioned receptors were available through rather tedious multistep synthesis

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(except cyclodextrins, prepared biochemically from the starch). Thus the overall yields were rather low, limiting, therefore, their potential applications as auxilliaries for the resolution of enantiomeric mixtures. Furthermore, the versatility of these receptors was also limited: crown ethers and cryptands could recognize cationic species, whereas cyclodextrins, neutral molecules. It is noteworthy that calixarenes the receptors prepared from phenols and aldehydes by an acid-catalysed condensation, can deliver an outstanding variety of the receptor structures that can, in principle, recognize cationic and anionic species, as well as neutral molecules, depending on the substituent attached to the pre-formed calixarene skeleton. The availability of modified calixarenes is much higher than in the case of other synthetic receptors. Calixarene chemistry has a very rich literature, including monographs [1, 2].

There has been an interest in the past concerning chiral calixarenes [3–27]: some reports dealt with inherently chiral calixarenes (no symmetry elements in the skeleton), some with chirality introduced by attaching the chiral unit.

There is a need to separate enantiomers and monitor the enantiomeric purity of commercial products, such as drugs, pesticides, food additives, *etc.*, and according to international regulations the use pure enantiomers is usually requested. Development of chiral receptors based on calixarenes, may provide not only new analytical tools for controlling the enantiomeric purity, but also a means for the separation of enantiomers. It should be noted that attractiveness of calixarenes relies on their possibilities to form the molecular cavities of various size and depth. This feature is particularly important for rational design and synthesis of specific receptors for particular molecules, or ions which differ in size, functionalities, and shape.

Molecular recognition phenomena can be followed by a number of methods, such as calorimetry, NMR and UV–Vis spectroscopy, electrochemical methods, mass spectrometry, X-ray analysis, and more recently, by Langmuir, or Langmuir–Blodgett techniques. Calixarenes have been shown to produce stable monolayers [28–38].

Ion binding properties of ionophores assembled in monolayers have been reported by several authors [31, 33–35, 37]. Complexing abilities of alkylated calix[4]resorcinarenes toward alkali metal cations in bulk solutions have been proved [39–42].

In the present work our aim was to compare the properties and organization of monolayers of three differently substituted C-undecylcalix[4]resorcinoarenes (Fig. 1) at the air–aqueous subphase interface.

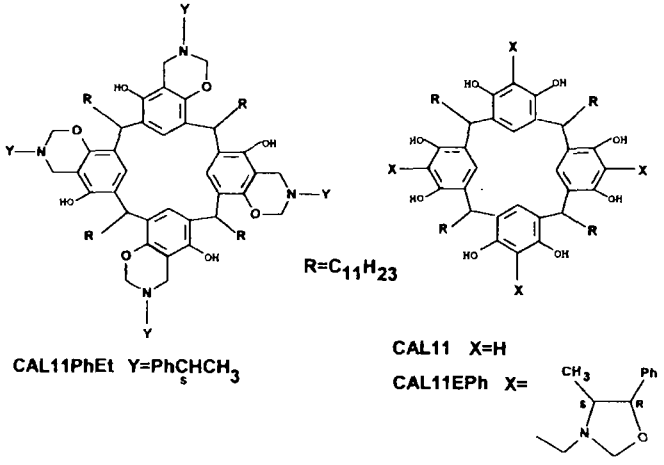

FIGURE 1 Structures of the compounds studied.

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The calix[4]resorcinarene has four important conformers: come, flattened partial cone, 1,3-alternate and flattened cone [1]. Monolayers of unsubstituted C-undecylcalix[4]resorcinarene have been studied by Aroca *et al.* [29, 31, 32]. We expected that conformational changes would have a pronounced effect in the case of calixarenes with large substituents such as L(−)norephedrine or phenylethyl groups. Since metal ions and small molecules are known to bind to calixarenes special attention is paid to the effects of the composition of the subphase upon the organization of the monolayer.

EXPERIMENTAL

Organic Synthesis

All compounds were obtained by described methods: unsubstituted C-undecylcalix[4]resorcinarene **1** by the method of Aoyama [42], the two chiral calix[4]resorcinarenes **2** and **3** by the method described by Böhmer [44]. All chemicals were purchased from Aldrich or Merck, and used as received.

Langmuir Film Studies

Surface pressure and surface potential *vs.* area per molecule isotherms were recorded using the computer controlled KSV-5000 with Wilhelmy plate type microbalance. Surface potential and surface pressure measurements were done simultaneously as a function of molecular area. Software version KSV 5000 was used. The instrument was placed in a laminar hood in which temperature was kept constant, $20 \pm 1°C$. The procedures of cleaning the trough and monolayer spreading have been described earlier [45–49]. The accuracy of measurements was $\pm 0.1\,mN\,m^{-1}$ for surface pressure, $\pm 1\,Å^2$ molecule^{-1} for molecular area and $\pm 5\,mV$ for surface potential.

All materials were of analytical grade. The solutions of molecules were prepared daily by dissolving 5 mg of the compound in 5 ml $CHCl_3$. Distilled water used as the subphase was passed through a Millipore-Q water purification system. Chloroform (Aldrich) was employed as the spreading solvent.

RESULTS AND DISCUSSION

Monolayers on the Air-Water Interface

Monomolecular layers of the three amphiphilic calixarenes (Fig. 2) were prepared initially on a pure water subphase. The characteristics of the isotherms is given in Table I.

The limiting areas per molecule in the monolayer are 1.68, 2.81 and 2.78 nm^2 for compounds CAL11, CAL11PhEt and CAL11Eph, respectively. The value for compound CAL11 is larger than predicted for the crown headgroup in the cone shape, 1 nm^2 [32]. The area reported for CAL5, CAL7 and CAL15 are 1.3, 1.6 and 2.2 nm^2, respectively [32]. These values point to the tilting of the hydrocarbon chain which changes with the increase of chain length and defines the area occupied by a molecule. As reported by Aroca [29] the conformation is not simply locked into a cone and a distribution of conformers may be present. The interaction with solvent may also change the relative orientation of aromatic rings. Binding of the chloroform Cl group in

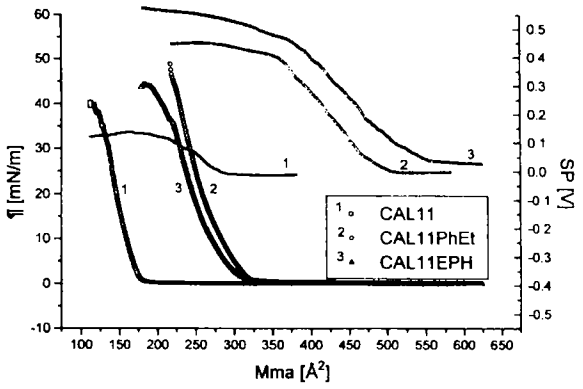

FIGURE 2 Surface pressure and surface potential – area isotherms for the compounds studied on a pure aqueous subphase 1. CAL11, 2. CAL11PhEt and 3. CAL11Eph.

TABLE I Characteristics of isotherms of the calix[4]resorcinarenes

Compound	Solution	A_0/solid [Å^2]	¶col [mN/m]	C_s^{-1} [mN/m]	ΔV [V] measured at max. packing 28 mN/m	μ [D]
CAL11	H_2O	168 ± 3	38	133 ± 3	0.125	0.45 ± 0.05
CAL11	KCl	173 ± 3	34	135 ± 3	0.167	0.64 ± 0.05
CAL11PhEt	H_2O	281 ± 3	30	161 ± 8	0.425	2.75 ± 0.20
CAL11PhEt	KCl	283 ± 9	35	130 ± 10	0.520	3.25 ± 0.18
CAL11Eph	H_2O	278 ± 6	40	146 ± 9	0.550	3.43 ± 0.20
CAL11Eph	KCl	263 ± 9	35	153 ± 9	0.478	2.83 ± 0.18

the cavity would be more effective if the cone is flattened. The shape of the surface-pressure isotherm depends on the size of the cavity and the nature of its substituent. When a bulky substituent is used such as L(−)norephedrine or phenylethyl, the area per molecule is distinctly larger than for the unsubstituted compound CAL11 (Tab. I), which indicates that the substituent determines the area occupied by the molecule on the air−water interface. The slope of the isotherms decrease upon substitution. Compressibility modulus, $C_s^{-1} = (A)(d\pi/dA)$, allows to obtain the information on the phases of the monomolecular films (Tab. I). The compressibilities of the monomolecular layers spread on water are depicted in Table I. The values correspond to that qualified as liquid condensed phase [50].

L(−)norephedrine or phenylethyl substitution leads to the increase of the surface potential of the monolayer formed at the air−water interface (Tab. I) which can be translated into the change of vertical component of the dipole density. The change of surface potential brought about by the formation of monolayer [51, 52] is given by:

$$\Delta V = V_M - V_R, \tag{1}$$

where V_M is measured in the presence and V_R without monolayer of calixarene. The potential jump at the air−water interface, ΔV, induced by the formation of monolayer is described by the Helmholtz equation:

$$\Delta V = 1/\epsilon_0 \times n \times \mu, \tag{2}$$

where n is the number of spread molecules, ϵ_0 is the permittivity in vacuum and μ is the effective dipole moment perpendicular to the surface. The values of surface potentials depicted in Tables I and II correspond to close to maximum packing of the monolayer which is assumed to be attained at surface pressure of 28 mN/m.

In our case [53, 54, 32]:

$$\Delta V = \Delta V_1 + \Delta V_2 = \mu_{ICH_3}/(\varepsilon_m \varepsilon_0 A) + \mu_{head}/(\varepsilon_w \varepsilon_0 A) \tag{3}$$

where ΔV_1 and ΔV_2 are the components of the surface potential corresponding to the alkyl tail and headgroup, respectively, μ_{ICH_3} and μ_{head} are the effective dipole moment of the hydrocarbon chain and of the headgroup, respectively, ε_w and ε_m are relative dielectric permittivities of water and of the molecular layer and A is molecular area. Using equation [32]:

$$\mu_{ICH_3} = 4\,\mu_{CH_3} \cos\Theta \tag{4}$$

and the values of the measured surface potential we deduced the average tilt of the four hydrocarbon chains. μ_{ICH_3} was taken 0.35 D following Nabok *et al.* [32] based on the calculation for a close-packed stearic acid monolayer. The tilt of the hydrocarbon chain in CAL11 and was found to be 66°.

Substitution of the molecule by phenylethyl or L(−)norephedrine groups leads to the perpendicular component of dipole moment ca. 6 times that of CAL11 as depicted in Table I. This

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TABLE II Limiting area per molecule and surface potential at maximum packing corresponding to 28 mN/m for the calixresorcinarene monolayers on subphase containing 10^{-4} M amino acids

Subphase	CAL11 A_0 [Å]^2	CAL11 C_s^{-1} mN/m	CAL11 ΔV[V] at max. packing at 28 mN/m	CAL11Ep A_0 [Å]^2	CAL11Eph C_s^{-1} mN/m	CAL11Eph ΔV[V] at max. packing at 28 mN/m	CAL11PhEt A_0 [Å]^2	CAL11PhEt C_s^{-1} mN/m	CAV11PhEt ΔV[V] at max. packing at 28 mN/m
l-trp	201 ± 7	155 ± 8	0.191	204 ± 4	170 ± 5	0.575	203 ± 4	90 ± 10	0.458
l-val	211 ± 5	157 ± 5	0.104	200 ± 6	149 ± 5	0.628	188 ± 5	124 ± 9	0.433
d-trp	206 ± 7	189 ± 7	0.100	214 ± 5	125 ± 4	0.574	267 ± 10	156 ± 8	0.353
d-val	209 ± 5	164 ± 5	0.121	238 ± 5	136 ± 6	0.463	202 ± 9	112 ± 8	0.430
dl-trp	204 ± 5	162 ± 5	0.170	200 ± 6	134 ± 5	0.572	202 ± 9	95 ± 10	0.430
dl-val	205 ± 5	169 ± 5	0.147	238 ± 8	107 ± 10	0.553	186 ± 7	140 ± 9	0.435
H_2O	168 ± 3	138 ± 3	0.125	278 ± 6	153 ± 9	0.550	281 ± 3	161 ± 4	0.425

exhibits that polar groups have been inserted into the molecule and have impact in the total dipole moment.

Effect of K^+ Ion in the Subphase on the Monolayer Properties

Figures 3a, b, c and Table I allow comparison of the effect of KCl in the subphase on the rigidity of the monolayer. For unsubstituted and phenyl-ethyl-substituted compounds the presence of KCl leads to higher perpendicular dipole moments and surface potentials while the mean molecular areas are not very different. The latter means that the polar headgroup interacts with the ion, the ion remains in the solution and does not increase repulsion between molecules in the monolayer, nor does it change the conformation of the molecules.

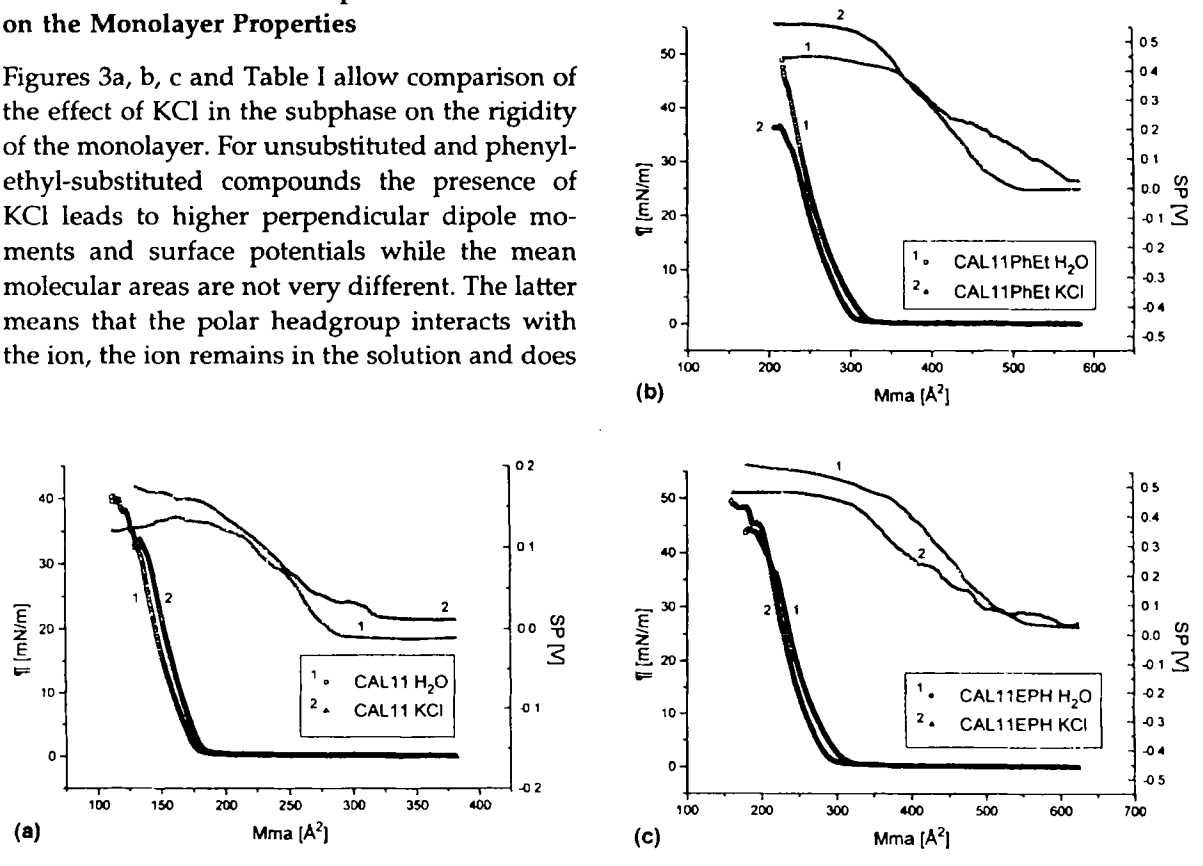

FIGURE 3 Comparison of surface pressure and surface potential – area isotherms on a pure aqueous and on 0.1 mol dm^{-3} KCl subphase. (a) CAL11; (b) CAL11PhEt and (c) CAL11Eph. 1. H_2O and 2. KCl subphase.

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Effects of Amino Acids upon the Properties of Langmuir Monolayers

For simple CAL11 the molecular areas in the monolayer increase when amino acids are introduced into the subphase [Fig. 4c]. This means that a more flattened conformation predominates. This may be explained assuming that the hydrogen bonding between multiple hydroxyl groups of the host molecules is weakened by the interactions with amino acids in the subphase. Amino acids also decrease the surface potential values of CAL11 at maximum packing of the monolayer (Tab. II). The decrease of surface potential can be understood in terms of increase of the effective dipole moment of the calixarenes head groups (Eq. 3) due to their interactions with amino acids in the solution and the resulting changes in the local dielectric permitivity. The compressibility factor does not practically change. For both the L(−)norephedrine- and phenylethyl-substituted calixarenes (Tab. II) the area occupied by a molecule of compound in the monolayer decreases in contact with a subphase containing amino acids [Figs. 4b–c]. Most probably, partial immersion of the substituent in the subphase is the result of interaction with the amino acids. Under these conditions substituents do not control the molecular area at the air–water interface and it becomes similar for all derivatives of CAL11 (Tab. I). The dipole moment also decreases for CAL11Eph and CAL11PhEt when any of the amino acids studied is present in the solution (Tab. III). It is of importance that more specific interactions seem to be induced by the functionalization of the calixarenes with the L(−)-norephedrine group. They are visualized by the large decrease of surface potential in the presence of D-isomers of the amino acids studied. Ca. 100 mV lower surface potential at maximum packing is seen in case of D-valine when norephedrine substituted calixarene is used to construct the responsive monolayer. Similarly, the phenylethyl derivative responds

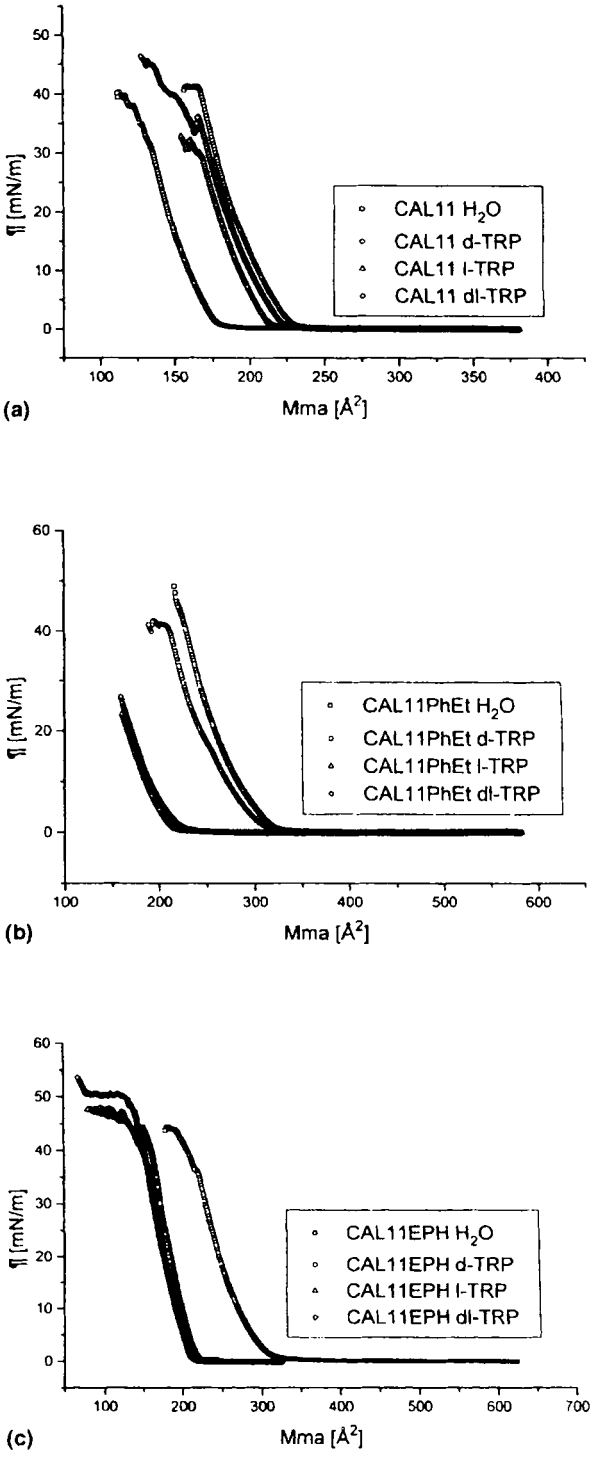
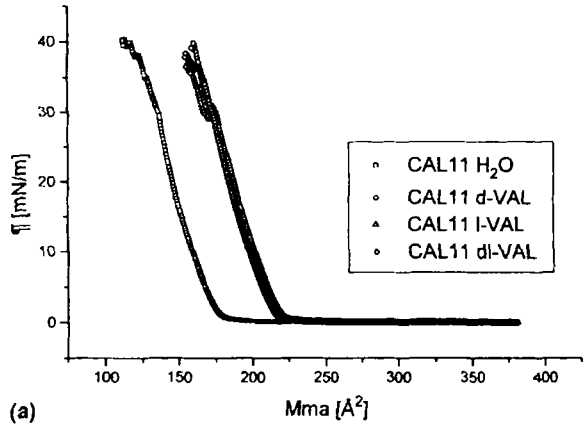


FIGURE 4 Dependence of surface pressure–mean molecular area on the isomer of tryptophan present in the subphase. (a) CAL11, (b) CAL11PhEt and (c) CAL11Eph.

TABLE III Perpendicular component of the dipolar moment calculated from surface potential at maximum surface packing taken as 28 mN/m

Subphase	CAL11 μ[D] at max. packing at 28 mN/m	CAL-PhEt μ[D] at max. packing at 28 mN/m	CAL-Eph μ[D] at max. packing at 28 mN/m
l-trp	0.85 ± 0.07	1.82 ± 0.09	2.64 ± 0.14
l-val	0.48 ± 0.06	1.75 ± 0.07	2.73 ± 0.08
d-trp	0.47 ± 0.07	2.13 ± 0.10	2.64 ± 0.16
d-val	0.56 ± 0.05	1.83 ± 0.12	2.52 ± 0.06
dl-trp	0.78 ± 0.05	1.82 ± 0.11	2.50 ± 0.12
dl-val	0.68 ± 0.06	1.76 ± 0.09	2.70 ± 0.11
H_2O	0.45 ± 0.05	2.75 ± 0.20	3.43 ± 0.20
KCl	0.64 ± 0.05	3.25 ± 0.18	2.83 ± 0.18



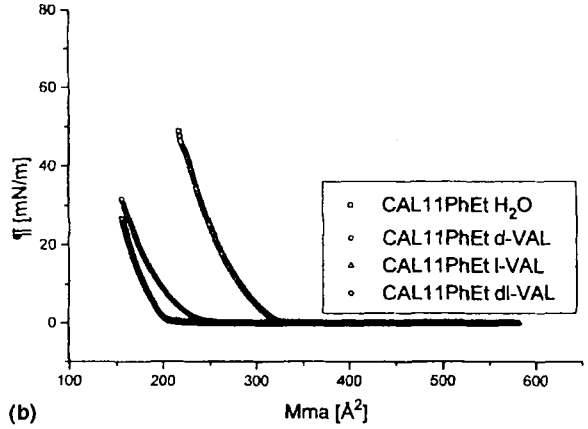


FIGURE 5 Dependence of surface pressure–mean molecular area isotherms for (a) CAL11, (b) CAL11PhEt and (c) CAL11Eph on the valine isomer present in the subphase.

to D-tryptophan. This is a pronounced indication of chiral recognition abilities of the modified calixresorcinarene molecules.

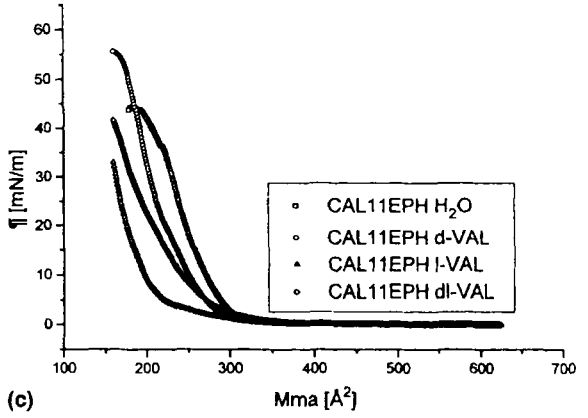


FIGURE 5 (Continued).

CONCLUSIONS

Molecular films of the calixarenes studied are able to form liquid condensed phases as deduced from the slopes of surface pressure–molecular area isotherms. Interactions of the molecules in the monolayer with solution resident ions (K^+) and neutral compounds (amino acids) were reflected by changes of surface potential and dipole moment. Interactions with amino acids lead also to conformational changes of the calixarenes exhibited by changes in the mean molecular area of the molecules in the monolayer.

Functionalisation of C-undecyl[4]resorcinarenes with L(−)norephedrine or phenylethyl substituent was shown to induce recognition properties of the monolayers of these molecules

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towards D- and L-amino acids. They were exhibited by a significant decrease of surface potential and dipole moment at the maximum packing of the monolayer when D-tryptophan or D-valine were added to the subphase.

Acknowledgments

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