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Macrocyclic amphiphiles. Part 2.†—Multi-point adsorptivity of the crown conformer of calix[4]resorcinarenes and their derivatives on surfaces of amorphous polar substrates

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The adsorption behavior of the crown conformer of calix[4]resorcinarenes (CRAs), cyclic tetramers of resorcinol and aliphatic aldehydes, and their *O*-carboxymethoxylated and *O*-hydroxyethyloxylated derivatives on a quartz surface was investigated. The adsorption of the macrocyclic amphiphiles from solutions of less polar solvents such as toluene at concentrations of $>10^{-3}$ mol dm^{-3} obeyed the Langmuir equation to give monomolecular layers. The absorption equilibrium constant for CRA was two orders of magnitude greater than that of the corresponding resorcinol. Such efficient adsorptivity of the macrocyclic compounds arises from their characteristic structures which possess eight hydrogen-donating polar residues on the same rim of the cylindrical molecular skeleton. CRA molecules are also adsorbed on the surface of a poly(vinyl alcohol) thin film, suggesting that these cyclic tetramers provide a general procedure to give monomolecular layers deposited on polar surfaces of amorphous solids.

Surface modification of solid materials has attracted interest not only from a practical standpoint, but also from a fundamental viewpoint since the nature and structures of solid surfaces determine crucially chemical as well as physical properties of materials participating in various interfacial phenomena.[1] Our work has revealed that photoactive molecular layers tethered to silica surfaces display dynamic phenomenon[2] leading to liquid crystal alignment photocontrol[3] as well as dispersion photocontrol of colloidal silica particles.[4,5] In order to proceed further, surface functionalization including molecular amplification stored by photochromic monomolecular layers,[2] and preparative methods to give tailor-made monomolecular layers deposited on solid surfaces, in particular, of amorphous substrates such as silica plates and polymer films are urgently required. Whereas the Langmuir–Blodgett technique provides versatile ways to modify solid surfaces with well-designed molecular films,[6] self-assembled monolayer (SAM) systems have being attracting ever increasing interest on account of their good availablility and wide applicability. SAMs are formed spontaneously by the immersion of a substrate plate into a solution of suitably polar molecules. Representative chemical species for the preparation of highly ordered SAMs involve silanes on silica,[7–9] alkanethiols on metals such as gold, silver and copper,[10–12] phosphonates on metal phosphonates,[13] carboxylic acids on metal oxides[14] and alcohols or amines on platinum.[15] Usually, a self-assembling molecule has a common structural feature consisting of a polar head group to bind to a substrate surface exothermally and a long-chain alkyl residue to enhance intermolecular interactions in SAM systems through the van der Waals force of polymethylene units. These requirements for assembling stable molecular films are in particular inevitable when surface binding is based on non-covalent bonds such as hydrogen bonds. As revealed by the pioneering work of Zisman *et al.*,[15] closely packed monolayers of aliphatic alcohols, amines and carboxylic acids are formed on surfaces of solids such as platinum only when the following requirements are fulfilled: there are critical chain lengths of surfactants, and no self-assembled monolayer is available when molecules are branched or incorporate functional group(s) such as an unsaturated double or triple bond in the straight alkyl chain. For our purpose to achieve the photocontrol of interfacial phenomena by tailor-made molecular films, photochromic units should be incorporated in self-assembling molecules. This situation does not allow us to employ conventional procedures to give SAMs through non-covalent bonds because the molecule bears a photofunctional unit and displays a drastic shape change accompanied by a marked sweep volume. We reported recently that no surface adsorption on a silica plate is achieved with amphiphilic azobenzenes having a carboxy or urethane residue whereas an aminoalkylated azobenzene adsorbs on a silica surface to enable us to assemble photoresponsive liquid crystal cells.[16] But this type of cell surface-modified with an aminoalkylated azobenzene becomes photoinactive after a while due to the desorption of the aminoazobenzene.

Calix[4]resorcinarenes (CRAs) **1**[17] are readily available by the condensation of an equimolar amount of resorcinol with the corresponding aldehyde in an acidic alcohol[18] and have been attracting interest due to their host–guest chemistry.[19–22] The crown conformer has eight hydrophilic residues on the same rim of the cylindrical molecular skeleton so that the macrocyclic molecules are expected to adsorb effectively on a polar silica surface from solution as a result of the cooperative interaction of the phenolic groups with surface silanols leading to multi-point adsorption. In particular, the crown conformer as a macrocyclic amphiphile is very attractive because the molecule consists of two parts of different cross-sectional areas. Examination with molecular models and π–A isotherm measurements have revealed that the lower base of the cyclic

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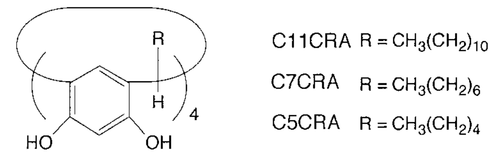
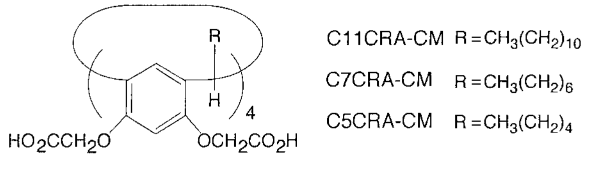
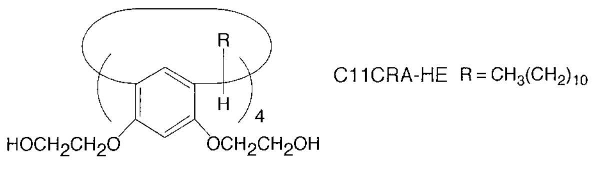
skeleton substituted with eight OH groups has a cross-section of *ca.* 1.3 nm^2, [23] while the cross-section of a sum of four alkyl chains derived from an aliphatic aldehyde attached to the lower rim is estimated to be *ca.* 0.88 nm^2 so that a two-dimensional free volume should be secured in a molecular film even though adsorption of the molecules on a surface is very dense. During the course of our work on surface modification with CRAs, it has been reported that multi-layers are readily deposited on solid surfaces by self-adsorption of a CRA having four alkyl residues in hexane solution.[24] The surface adsorption of the CRA on a quartz plate to form a multi-layer has been suggested though detailed adsorption behavior has not yet been reported. We have recently observed that a CRA substituted with azobenzene residues at the same rim of the cyclic skeleton absorbs on a colloidal silica surface to give rise to dispersion photocontrol owing to the photoisomerization of surface molecules.[5] The major purpose of this paper is to show the effectiveness of multi-point adsorptivity of CRAs and their derivatives on polar surfaces of amorphous solid to form monomolecular layers from less polar solutions.







Experimental

Materials

Calix[4]resorcinarenes. Calixresorcinarenes were prepared by the condensation of resorcinol with the corresponding aliphatic aldehydes according to the literature.[18,20] The crown structure was confirmed by NMR spectroscopy. 4-Undecylresorcinol was used as received.

***O*-Octacarboxymethylated calix[4]resorcinarenes (C*n*CRA-CM) (3).** 2,8,14,20-Tetraundecyl-4,6,10,12,16,18,22,24-octacarboxymethoxycalix[4]arene (C11CRA-CM) is a typical example: to 10 ml of DMF was added 1.0 g of the crown conformer of the cyclic tetramer of resorcinol and dodecanal (octadodecylcalix[4]resorcinarene; C11CRA), 2.0 g of anhydrous potassium carbonate and 2.38 g of ethyl bromoacetate. The mixture was heated at 80 °C for 6 h under magnetic stirring, followed by treatment with a mixture of diethyl ether and water to separate the organic layer. After washing with saturated aqueous NaCl and drying over magnesium sulfate, the diethyl ether was removed to obtain a viscous residue. This was subjected to silica gel column chromatography using a 2:3 mixture of ethyl acetate and hexane to isolate 1.55 g (68.6% yield) of the *O*-octa(ethoxycarbonylmethoxymethylated) C11CRA (C11CRA-EM) as needle-like crystals of mp 30–31 °C. δ_H ($CDCl_3$) 0.88 (12H, t, CH_3), 1.0–1.4 (96H, br, $-CH_2-$ and $-COOCH_2CH_3$), 1.83 (8H, CH_2), 4.0–4.4 (32H, br, Ar$-OCH_2COOCH_2CH_3$), 4.60 (4H, t, Ar$-$CRH$-$Ar), 6.24 (4H, s, Ar-H), 6.62 (4H, s, Ar-H). The octaester (3.0 g) was dissolved in 20 ml of ethanol, and 1.5 g of potassium hydroxide was added. During 2 h stirring of the solution at 60 °C, distilled water was periodically added to dissolve any colorless precipitates. The alkaline solution was acidified with hydrochloric acid to precipitate a white substance which was extracted with diethyl ether. The organic layer was washed with saturated aqueous NaCl and dried over magnesium sulfate. After removal of the solvent by evaporation the residue was C11CRA-CM, a colorless solid (1.93 g; 71.7% yield), mp 173–175 °C. δ_H ([$^2H_6$]DMSO at 50 °C) 0.82 (12H, t, CH_3), 1.2 (72H, br, $-CH_2-$), 1.8 (8H, br, $-CH_2-$), 4.1–4.7 (20H, br, Ar$-$CRH$-$Ar, Ar$-OCH_2COOH$), 6.39 (4H, s, Ar-H), 6.55 (4H, s, Ar-H), 12.51 (8H, br s, COOH) (Found: C, 65.88; H, 8.43. Calc. for $C_{88}H_{128}O_{24}+2H_2O$: C, 65.81; H, 8.28%).

Similarly, 2,8,14,20-tetraheptyl-4,6,10,12,16,18,22,24-octacarboxymethoxycalix[4]arene (C7CRA-CM), mp 148–150 °C, was obtained in 39.4% yield. δ_H ([$^2H_6$]DMSO at 50 °C) 0.82 (12H, t, CH_3), 1.2 (40H, br, $-CH_2-$), 1.8 (8H, br $-CH_2-$), 4.1–4.7 (20H, br, Ar$-$CRH$-$Ar, Ar$-OCH_2COOH$), 6.39 (4H, s, Ar-H), 6.55 (4H, s, Ar-H), 12.5 (8H, br s, COOH) (Found: C, 63.64; H; 7.55. Calc. for $C_{72}H_{96}O_{24}+H_2O$: C, 63.42; H, 7.24%).

2,8,14,20-Tetrapentyl-4,6,10,12,16,18,22,24-octacarboxymethoxycalix[4]arene (C5CRA-CM), mp 181–182 °C, was obtained in 98.3% yield. δ_H ([$^2H_6$]DMSO at 50 °C) 0.81 (12H, t, CH_3), 1.3 (24H, br, $-CH_2-$), 1.8 (8H, br, $-CH_2-$), 4.0–4.6 (20H, br, Ar$-$CRH$-$Ar, Ar-OCH_2COOH), 6.38 (4H, s, Ar-H), 6.54 (4H, s, Ar-H), 12.5 (8H, br s, COOH) (Found: C, 61.61; H, 6.52. Calc. for $C_{64}H_{80}O_{24}+H_2O$: C, 61.43; H, 6.61%).

2,8,14,20-Tetrapropyl-4,6,10,12,16,18,22,24-octacarboxymethoxycalix[4]arene (C3CRA-CM), mp 209–211 °C, was obtained in 98.1% yield. δ_H ([$^2H_6$]DMSO at 50 °C) 0.89 (12H, t, CH_3), 1.3 (8H, br, $-CH_2-$), 1.8 (8H, br, $-CH_2-$), 4.0–4.8 (20H, br, Ar$-$CRH$-$Ar, Ar$-OCH_2$ COOH), 6.41 (4H, s, Ar-H), 6.60 (4H, s, Ar-H), 12.50 (8H, br s, COOH) (Found: C, 57.98; H, 5.78. Calc. for $C_{56}H_{64}O_{24}+2H_2O$: C, 58.13; H, 5.92%).

2,8,14,20-Tetraundecyl-4,6,10,12,16,18,22,24-octa(2-hydroxyethoxy) calix[4]arene (C11CRA-HE) (5). To a suspension of $LiAlH_4$ (LAH) in dry THF was added dropwise a solution of the octa(*O*-ethoxycarbonylmethylated) C11CRA (C11CRA-EM) in 20 cm^3 of THF under stirring. After stirring for 1 h, the excess of LAH was reacted with ethyl acetate, and the reaction mixture was treated with saturated aqueous ammonium chloride. The organic layer was separated; removal of the solvent gave a residual solid which was recrystallized from methanol to give colorless leaflets of mp 192–193 °C, 0.23 g (56.1% yield). δ_H ($CDCl_3$) 0.86 (12H, t, CH_3), 1.2 (72H, br, $-CH_2-$), 1.8 (8H, br, $-CH_2-$), 2.85 (8H, s, OH), 3.5–4.2 (32H, br, $-OCH_2CH_2OH$), 4.49 (4H, t, Ar$-$CRH$-$Ar), 6.28 (4H, s, Ar$-$H), 6.69 (4H, s, Ar$-$H) (Found: C, 71.00; H, 10.07. Calc. for $C_{88}H_{144}O_{16}+2H_2O$: C, 70.74; H, 9.98%).

Surface adsorption experiments

Quartz plates (1 × 3 cm^2) were washed in a mixture of acetone, THF and methanol ultrasonically and dried at 120 °C. They were treated ultrasonically with conc. nitric acid, deionized water, aqueous sodium hydrogen carbonate and finally with deionized water, and used immediately. Surface adsorption of CRA derivatives or the model compound, 4-undecylresorcinol (C11-Res), was carried out just after drying at 120 °C by immersing a clean quartz plate in a solution (10 ml) of the adsorbate placed in a thermostatted bath with gentle shaking. The plate was rinsed with toluene briefly and dried at 120 °C before being subjected to the UV absorption spectral measurements (Fig. 1) using a Hitachi UV-320 spectrometer to evaluate the amount of the adsorbate (W = molecules per nm^2)

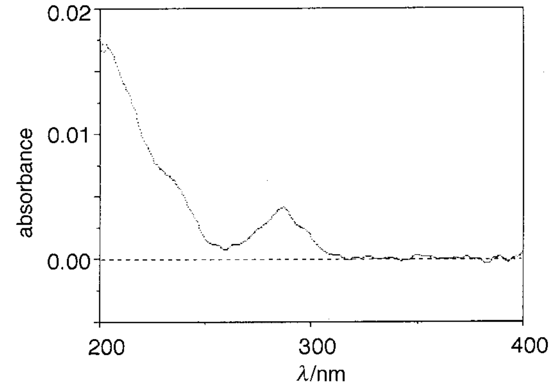


Fig. 1 UV spectrum of C11CRA adsorbed on a quartz plate

according to eqn. (1),

$$W = 6.02 \times 10^6 \times A/2\varepsilon \qquad (1)$$

where A and ε ($= 1.82 \times 10^4$ dm^3 mol^{-1}) denote the absorbance at λ_{max} and the absorption coefficient, respectively.

UV absorbances are small so an absorption spectrum of the same plate was taken prior to the adsorption experiment as a reference to obtain the spectrum of CRA adsorbed on the plate. The amounts of adsorbed CRA and its derivatives were determined three times by measuring absorbances at λ_{max}. Plates were coated with a poly(vinyl alcohol) film and handled under a nitrogen atmosphere after the adsorption experiment in order to avoid deterioration of the film surface due to moisture.

Adsorption on colloidal silica

Silica particles donated by Tokuyama Co were mono-dispersed particles (0.40 µm diameter) with a BET nitrogen specific surface area of 6.1 m^2 g^{-1}. Prior to adsorption experiments, they were dried under vacuum at 180 °C for 5 h. A standard solution of a dry toluene solution of C11CRA (20 ml) was mixed with 1.00 g of silica particles in a glass tube and shaken gently at 25 °C for approximately 8 h to reach adsorption equilibrium. The silica suspension was centrifuged at 3000 rpm for 15 min to sediment silica particles, and the supernatant was removed and diluted with THF to monitor the concentration of the cyclotetramer spectroscopically. The amount of C11CRA adsorbed on flocculated silica, W_i (mmol g^{-1}), was calculated from eqn. (2),

$$W_i = V(C_o - C_i)/M_i \qquad (2)$$

where V = volume of a solution in ml, C_o = initial concentration of C11CRA in mol dm^{-3}, C_i = concentration of C11CRA in the supernatant after centrifugation in mol dm^{-3} and M_i = silica mass in g, respectively.

π–A curve measurement

Surface–pressure area isotherms were obtained by using a film balance, FSD-110 (USI Co, Ltd). The CRA derivative was spread on pure water, purified by Milli-Q, from a chloroform solution of the compounds (*ca.* 10^{-4} mol dm^{-3}).

Results and Discussion

Adsorption isotherms of CRAs

Preliminary results indicated that CRA molecules form multilayers on silica plates, judging from UV absorbances of plates immersed in more concentrated solutions (higher than a few 10^{-3} mol dm^{-3}); UV absorbances of the plates due to C11CRA were much larger than that of the plate treated with a more dilute solution. Anomalous adsorption behavior at higher concentrations of C11CRA was also observed using colloidal silica particles suspended in toluene solutions of the cyclotetramer. The suspension was subjected to centrifugation to separate the particles before UV absorption measurement of the supernatant, as this procedure gave more precise data because it does not involve surface washing and enables one to obtain much larger absorbances of CRA. As shown in Fig. 2, the amount of the adsorbate levels off in the concentration range from *ca.* 3×10^{-4} to *ca.* 2.0×10^{-3} mol dm^{-3}. This suggests that a monomolecular layered adsorption may take place at concentrations much lower than 2.0×10^{-3} mol dm^{-3}.

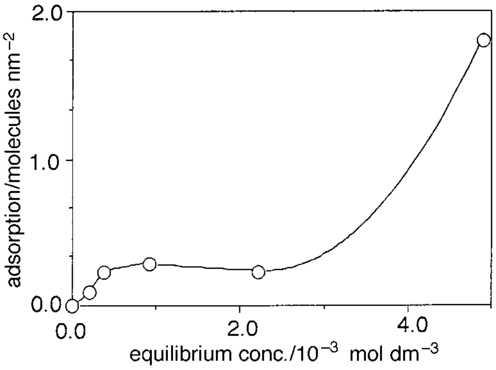


Fig. 2 Adsorption isotherms of C11CRA on colloidal silica in toluene at 25 °C

It has been reported that CRA molecules attached by gold–thiol covalent bonds form multi-layers of the cyclic compounds spontaneously owing to the cooperative action of intermolecular hydrogen bonds and interdigitation of hydrophobic alkyl chains.[24] It has also been reported briefly that this kind of multi-layer is also deposited on a quartz plate when C11CRA is dissolved in dichloromethane at a concentration of 10^{-3} mol dm^{-3}. This report is in line with our present results.

Based on these facts, adsorption experiments on quartz plates were carried out in dilute toluene solutions ($\ll 1 \times 10^{-3}$ mol dm^{-3}) in order to ensure monolayer adsorption. The number of adsorbed molecules per unit was estimated from the UV absorbance of C11CRA (Fig. 1). Fig. 3 shows the adsorption behavior of C11CRA in dilute toluene solutions of 1×10^{-4} and 1×10^{-5} mol dm^{-3} concentrations, respectively. Care was taken in the estimation of the amount of adsorbate on silica by means of UV absorbance measurements since desorption took place even upon washing of the surface-treated silica plates in fresh toluene with shaking, as shown in Fig. 4. In order to gain reproducible results, surface-adsorbed plates were rinsed for a few seconds in fresh toluene to remove the solution containing the adsorbates, and immediately dried. As seen in Fig. 3(*a*), the adsorption takes place slightly faster at 50 °C in a 10^{-4} mol dm^{-3} solution and levels off within several minutes. Temperature dependence of the adsorption was clearly observed when a more dilute solution (1×10^{-5} mol dm^{-3}) was used [Fig. 3(*b*)]. The adsorption was saturated within several minutes again at 50 °C though it occurred more slowly at 25 °C.

Fig. 5 shows the absorption isotherms of C11CRA and the model compound, 4-undecylresorcinol, in toluene at 25 °C. It is clearly seen that the adsorption is complete in very dilute solutions of the CRA derivatives compared with that of the model compound. The results displayed in Fig. 5 were analysed using the Langmuir formula, eqn. (3),

$$C/W = (1/a\ W_s) + (1/W_s) \times C \qquad (3)$$

where W and W_s are quantities in molecules per nm^2 of CRA at a concentration C in mol dm^{-3} and a saturated amount of the adsorbate, respectively, while a denotes the adsorption equilibrium constant in dm^3 mol^{-1}. The Langmuir plots for C11CRA and the model compound are given in Fig. 6. In both

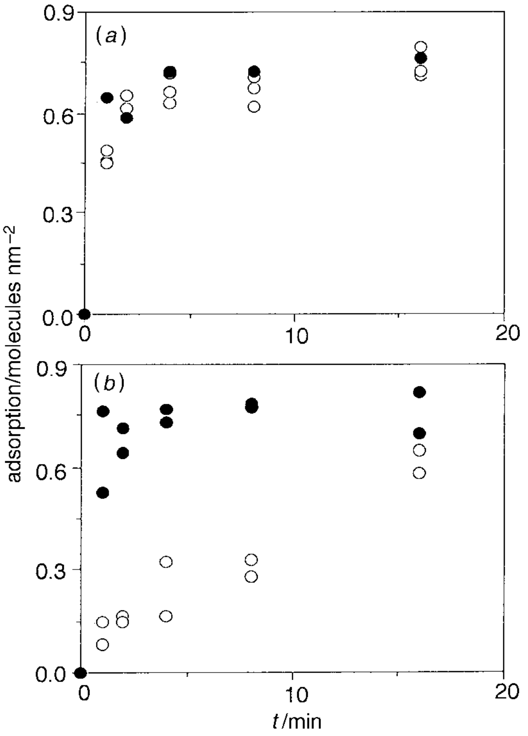


Fig. 3 Adsorption kinetics of C11CRA from toluene solutions of (*a*) 1×10^{-4} and (*b*) 1×10^{-5} mol dm^{-3}, respectively, at (○) 25 and (●) 50 °C

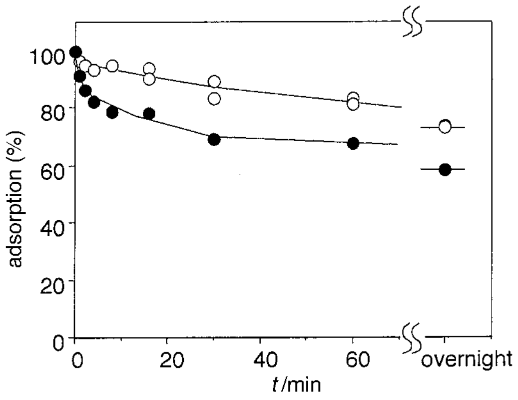


Fig. 4 Desorption of C11CRA from a quartz plate immersed in fresh toluene solutions at (○) 25 and (●) 50 °C, respectively

cases, a good linear relationship was obtained, which allowed us to estimate values of *a* and W_s summarized in Table 1. The enhancement of the adsorption owing to the effective multi-point adsorptivity was unequivocally revealed by the comparison of the adsorption equilibrium constant *a* for C11CRA and C11-Res. It should be stressed here that *a* for C11-CRA is about two orders of magnitude greater than that for C11-Res, as summarized in Table 1.

Table 1 also shows the saturated amount (W_s) of CRA on a quartz surface. The occupied area expressed as a reciprocal of W_s is calculated to be *ca.* 1.3 nm^2. According to a space-filling CPK model, the area of the base of CRA was *ca.* 1.3 nm^2 and coincides with the occupied area on silica within experimental error.

Furthermore, the π–A curve of the CRA was recorded in pure water to estimate the cross-sectional area of the cyclic compound [Fig. 7(*a*)]. It was *ca.* 1.4 nm^2 per molecule. This value of the base area (1.3–1.4 nm^2) is in line with the occupied area of C11CRA adsorbed on silica suggesting that the CRA molecules are placed on the surface two-dimensionally with a dense packing, as illustrated in Fig. 8.

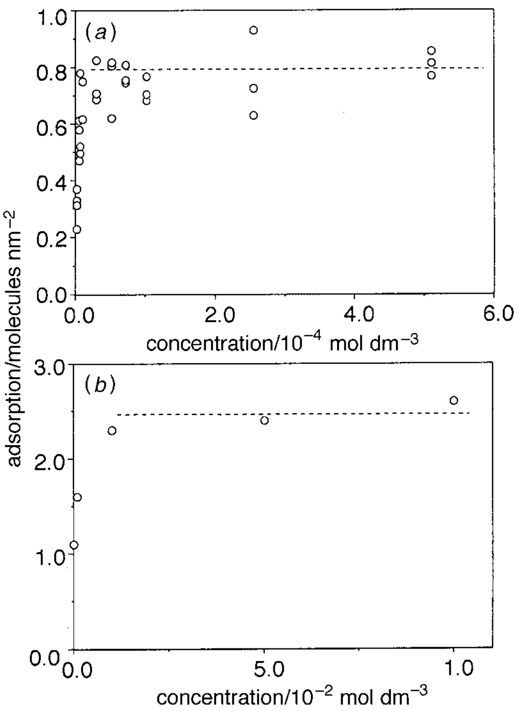


Fig. 5 Adsorption isotherms of (*a*) C11CRA and (*b*) C11-Res on a quartz surface from a toluene solution at 25 °C

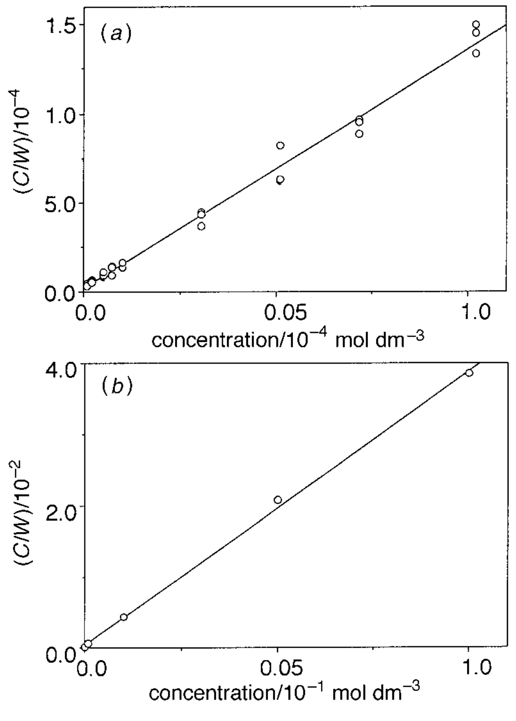


Fig. 6 Langmuir plots for (*a*) C11CRA and (*b*) C11-Res in toluene at 25 °C

The adsorption process may occur as follows. It has been shown that CRAs form molecular aggregates in solution owing to effective hydrogen bond formation.[19] In other words, there is an equilibrium between the monomeric form and the aggregated forms. As stated above, CRA possesses eight phenolic OH groups, which consist of four pairs forming intermolecular hydrogen bonds,[19] and monomeric CRA adsorbs on the silica surface through multi-point hydrogen bonds. It was reported that silanol residues are located on the surface at a density of 2.1–4.1 per 1 nm^2 of fused colloidal silica particles while fully hydroxylated silica is covered with 4.9 silanol residues per nm^2.[25] This means that one CRA molecule with a base

Table 1 Parameters for adsorption of CRA derivatives

CRA derivative	substrate	$T/°C$	a^a	W_s^b	S^c	solvent^d
C11CRA	silica plate	18	4.1×10^5	0.72 ± 0.01	1.39 ± 0.02	Tol
C11CRA	silica plate	25	4.4×10^5	0.75 ± 0.02	1.33 ± 0.03	Tol
C11CRA	silica plate	50	2.4×10^6	0.77 ± 0.01	1.30 ± 0.02	Tol
C11CRA	silica plate	50	3.3×10^6	0.77 ± 0.01	1.30 ± 0.02	Chl
C11CRA-CM	silica plate	25	3.0×10^6	0.64 ± 0.01	1.56 ± 0.02	Tol-THF
C11CRA-CM	silica plate	50	7.4×10^6	0.58 ± 0.03	1.72 ± 0.09	Tol-THF
C7CRA-CM	silica plate	25	1.6×10^6	0.63 ± 0.01	1.59 ± 0.02	Tol-THF
C7CRA-CM	silica plate	50	4.3×10^6	0.59 ± 0.03	1.69 ± 0.08	Tol-THF
C5CRA-CM	silica plate	25	—	0.63 ± 0.03	1.59 ± 0.07	Tol-THF
C5CRA-CM	silica plate	50	1.8×10^6	0.63 ± 0.02	1.59 ± 0.05	Tol-THF
C11CRA-HE	silica plate	50	9.8×10^6	0.59 ± 0.01	1.69 ± 0.03	Chl
C11CRA	PVA film	25	1.1×10^5	0.50 ± 0.01	2.00 ± 0.04	Tol
C11CRA	PVA film	50	8.0×10^4	0.59 ± 0.01	1.69 ± 0.03	Tol
C11-Res	silica plate	18	7.6×10^2	3.1 ± 0.3	0.32 ± 0.03	Tol
		25	8.7×10^2	2.4 ± 0.1	0.42 ± 0.02	Tol

[a] Equilibrium adsorption constant in $dm^3\ mol^{-1}$. [b] Saturated adsorption amount (molecules nm^{-2}) estimated from adsorption isotherm. [c] Occupied area (nm^2 per molecule). [d] Tol = toluene, Tol–THF = a 80:20 (v/v) mixture of toluene and THF, Chl = chloroform.

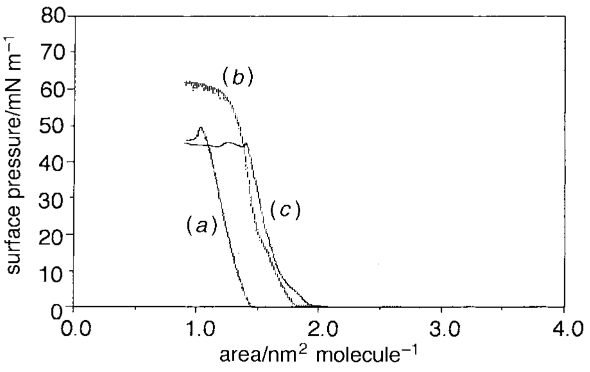


Fig. 7 Surface pressure area isotherms of (*a*) C11CRA, (*b*) C11CRA-CM and (*c*) C11CRA-HE on pure water at 25 °C, respectively

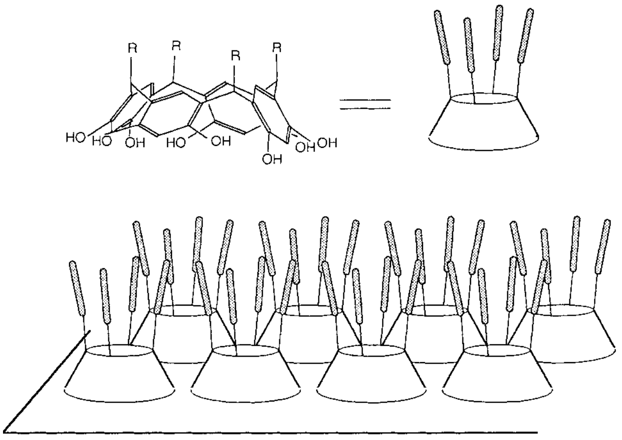


Fig. 8 Illustrative representation of adsorbed monolayers of a calix[4]resorcinarenes on a quartz plate surface

area of *ca.* 1.3 nm^2 has four to six silanols on a silica surface for hydrogen bond formation. But it is reasonable to say that silanol residues are distributed on a silica surface randomly because of its amorphous nature. Consequently, it is very likely that the number and location of hydrogen bonds formed between CRA and the surface are randomly distributed. This means that the binding strength of CRA on the surface is not uniform. As seen in Fig. 4, the desorption of the CRA occurs partially at the early stage of the washing out in fresh toluene, followed by a marked reduction in desorption rate. About 70 and 60% remain adsorbed on the surface at 25 and 50 °C, respectively, even after shaking overnight. This kind of desorption behavior may reflect the variable binding strength of CRA molecules on a silica surface. The desorption behavior indicates furthermore that the surface adsorption takes place reversibly. This reversible process of adsorption plays a crucial role in the formation of a densely packed monomolecular layer.

Adsorption of C11–CRA on PVA films

As an extension of the preparation of monomolecular layers by surface adsorption from a solution, a thin film of poly(vinyl alcohol) (PVA) was employed as a substrate, taking into account the ability of hydrogen bonds to form due to the OH groups of vinyl alcohol units. Silica plates were spin-cast with an aqueous solution of PVA to cover them with a thin film of the water-soluble polymer. The plates were immersed in toluene solutions of C11CRA for the adsorption experiment, in the same manner as used for the adsorption on a silica surface. Adsorption isotherms of C11CRA on PVA films are given in Fig. 9. We observed again that the CRA is adsorbed on the surface effectively. The results are plotted using the Langmuir equation to give W_s and a. These values are summarized in Table 1. When compared with the adsorption on a silica surface, the adsorption equilibrium constant a for a PVA film is considerably reduced at both 25 and 50 °C. This may arise from the weaker acidity of alcoholic OH groups. W_s values are also smaller for a PVA surface than for a silica surface. Thus, occupied areas of the CRA on a PVA surface are *ca.* 1.5 and *ca.* 1.7 nm^2 at 25 and 50 °C, respectively. It was reported that the surface of a PVA thin film is covered with *ca.* three OH groups per nm^2.[26,27] This OH density is slightly lower than that of silanol on silica so that the surface densities of CRA are reduced. It is noteworthy that the surface density becomes lower when the adsorption from a toluene solution is carried

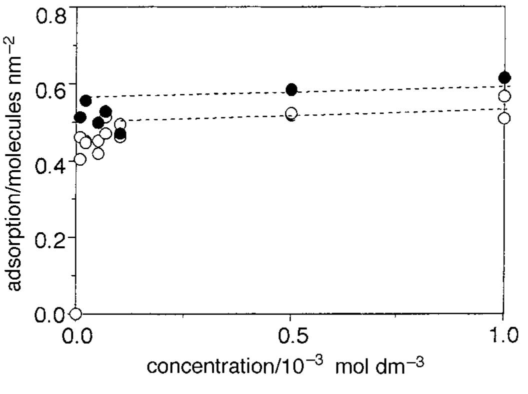


Fig. 9 Adsorption isotherms of C11CRA on a thin film of poly(vinyl alcohol) from a toluene solution at (○) 25 and (●) 50 °C

out at a higher temperature although the data contain experimental errors. It is frequently observed that polar side chains of polymers are subjected to inversion to decrease the surface energy when a surface is exposed to a phase of low polarity.[28] This kind of dynamic surface event may take place here. The increase in the occupied area at 50 °C is probably due to the inversion of polar OH groups exposed to the surface upon contact with a non-polar solvent to reduce the surface density of the OH groups.

Adsorption behavior of modified CRAs

As stated above, the two-dimensional surface density of C11CRA deposited on silica by adsorption is primarily determined by the area of the base of the CRA framework. This has led us to adjust the surface density of adsorbed CRA by the chemical modification of phenolic hydroxy groups. The key materials are *O*-ethoxycarbonylmethylated derivatives that were hydrolysed to give the corresponding *O*-carboxymethylated CRAs (CRA-CM), while an *O*-hydroxyethylated CRA (C11CRA-HE) was prepared by the reduction of the corresponding octaester derivative. The strong affinity of all of these derivatives for a silica surface was first confirmed by the lack of mobility of their spots on silica gel TLC plates with use of non-polar solvents as eluents. The adsorption isotherms for the carboxymethylated CRAs were examined in 80:20 (v/v) toluene–THF because of their slight solubility in pure toluene. They all exhibited the typical Langmuir-type adsorption to give W_s and a values summarized in Table 1. The adsorption of C11CRAHE was performed from a chloroform solution because of its slight solubility in toluene (Fig. 10). The adsorption is again of Langmuir type to give a and W_s. Although the values of equilibrium constant (a) are lacking in accuracy because of the scattered experimental data, it is safe to say that the equilibrium constants of *O*-carboxymethylated CRAs are not far from those of C11CRA, though the solvent contains the slightly polar THF, irrespective of the alkyl chain length, indicating the effectiveness of the octacarboxyl residues in the surface adsorption of this type of macrocyclic amphiphiles. In the case of the CRA-CM series, though the equilibrium constants do not differ significantly, the values increase with the increase in the chain length of alkyl residues. This is probably due to a hydrophobic interaction of alkyl chains.

The areas of the base of the cylindrical moieties of these compounds were estimated by measuring the π–A isotherms at an air–water interface. As seen in Fig. 7, in contrast to the case of C11CRA, π–A curves of both C11CRA-CM and C11CRA-HE possess breaks at *ca.* 20 and at *ca.* 10 mN m^{-1}, respectively, possibly reflecting the conformational alteration of hydrophilic residues during the compression at an air–water interface. Extrapolation of the curves of the early stage of compression gives occupied areas of 1.8 and 2.0 nm^2 per molecule for C11CRA-CM and C11CRA-HE while the steeper curves after the breaks lead us to the estimation of cross-sectional areas of 1.6 and 1.8 nm^2 per molecule, respectively. As the molecular models tell us, the substitution of carboxymethyl and hydroxyethyl residues at phenolic OH groups results in an enlargement of the base area of the cyclic compounds; C11CRA-CM and C11CRA-HE possess occupying areas of *ca.* 1.7 and *ca.* 1.8 nm^2, respectively. These areas are in accord with those of the corresponding adsorbed molecules within experimental error (Table 1). These facts again support the fact that the modified CRAs adsorb on a silica surface with dense two-dimensional packing, as shown in Fig. 8.

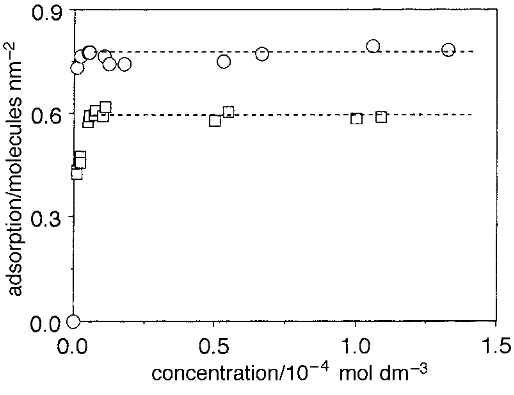


Fig. 10 Adsorption isotherms of (○) C11CRA and (□) C11CRA-HE in chloroform at 50 °C

Desorption of CRA derivatives from a silica surface

As presented in Fig. 4, the partial desorption of C11CRA from silica takes place even in toluene. Considering the importance of the stability of surface adsorption from a practical view of surface modification of silica surfaces, the desorption behavior of the C11-CRA derivatives was examined by the immersion of surface-modified quartz plates in various solvents at 25 °C. The extent of the desorption is plotted tentatively against a solvent polarity parameter (E_T value).[29] The results in Fig. 11 may be summarized as follows. First, the desorption of both of C11CRA and C11CRA-HE is enhanced by an increase in solvent polarity. Complete desorption of C11CRA-HE was induced by immersing a plate in acetone as well as methanol, suggesting that these solvents act as hydrogen bond acceptors to accelerate the desorption. In marked contrast to this, about 20% of C11-CRA remains adsorbed even after treatment with acetone or methanol. The desorption is not complete until a surface-treated plate is rinsed out with methanol containing octylamine as a strong hydrogen bond acceptor. This is probably due to the difference in the number of adsorption sites of CRA molecules on the silica surface. As mentioned above, the area of the base having eight OH groups at the upper rim is around 1.3 nm^2 so that each C11CRA molecule has a chance to make roughly four or five hydrogen bonds between it and the surface at most. Thus, the binding energy is at a maximum in a range of about 20 kcal mol^{-1}, offering relatively strong affinity for molecules generating cooperative hydrogen bonding owing to the matching of adsorption sites. Second, C11CRA-CM possesses stronger adsorptivity. Essentially no desorption was observed in non-polar solvents such as toluene, although the majority of molecules (*ca.* 75%) are desorbed from a silica surface in methanol. This implies that the CRA-CM family is a good candidate for forming a single monomolecular layer covering a silica surface simply by immersion in non-polar solvents.

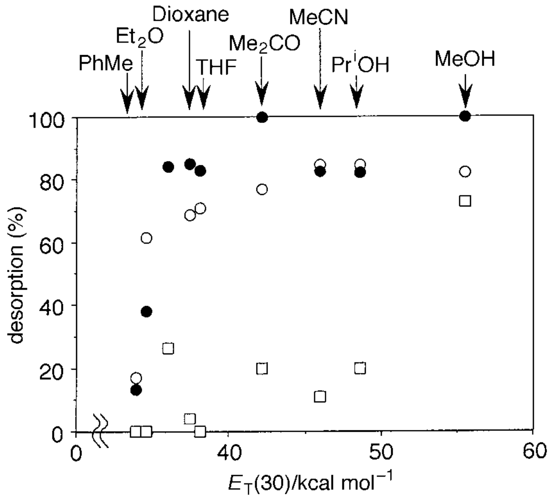


Fig. 11 Desorption of (○) C11CRA, (●) C11CRA-CM and (□) C11CRA-HE adsorbed on quartz plates, respectively, which were immersed in solvents with various E_T values

Conclusion

The present results are summarized as follows.

(1) The surface adsorption of CRA and its derivatives dissolved in toluene was followed by measuring their absorbances on substrate plates. In the range of concentrations of less than *ca.* 2.0×10^{-3} mol dm^{-3} of CRA derivatives, the macrocyclic amphiphiles are adsorbed onto polar surfaces of amorphous substrates such as silica glass to give saturated levels which correspond to cross-sectional areas determined by the base areas of the cyclic molecular frameworks. Occupied areas of CRAs were estimated by measuring surface pressure–area isotherms at an air–water interface and modulated by the chemical modification of hydrophilic units at the upper rim of the macrocycles. While the occupied area of CRAs is about 1.4 nm^2 per molecule, the *O*-methoxycarbonylmethylation and the *O*-hydroxyethoxylation of the eight phenolic residues expand the area of the CRA framework up to 1.8 and 2.0 nm^2, respectively. These values are approximately in line with the values of occupied areas adsorbed CRA derivatives.

(2) The surface adsorption of CRAs takes place even in highly dilute solutions with concentrations in the region of *ca.* 10^{-5} mol dm^{-3} and is accelerated by increasing the solution temperature. The adsorption isotherms nicely follow Langmuir plots to give adsorption equilibrium constants and saturated amounts of adsorbates. It was found that the adsorption equilibrium constant for C11CRA is roughly two orders of magnitude larger than that for the model compound, 4-undecylresorcinol. This supports the validity of the concept of multi-point adsorption to enhance the adsorption efficiency of macrocyclic amphiphiles to prepare monomolecular films on polar surfaces by a simple immersion procedure. This technique was applied to cover a surface of PVA thin films with a CRA monomolecular layer owing to multi-site formation of hydrogen bonds between cyclic molecules and a polar surface.

(3) The desorption of adsorbates was dependent on the nature of the solvent and the structure of hydrophilic residues of CRA derivatives. The removal of surface molecules is caused by immersion in polar solvents, and the extent of the desorption was in the following order; CRA-HE > CRA > CRA-CM. Eight carboxymethoxy residues are most effective for the surface adsorption in the surface modification of amorphous substrates.

This indicates that the surface adsorption of CRAs and their derivatives offers a promising method to obtain monomolecular layers on polar surfaces of amorphous solids such as silica and PVA simply by immersing substrate plates in a solution of the adsorbates in less polar solvents.

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