

Influence of Molecular Organization of Photo-active Azo-phanes on the Reactivity in Monolayers at the Air–Water Interface

H. HUESMANN¹, H. FUJIWARA^{1,2}, E. LUBOCH³, J.F. BIERNAT³ and D. MÖBIUS^{1*}

¹Max-Planck-Institut für biophysikalische Chemie, D-37070 Göttingen, Germany; ²Faculty of Information Sciences, Hiroshima City University, Hiroshima, 731-3194 Japan; ³Faculty of Chemistry, Gdańsk University of Technology, 80-952 Gdańsk, Poland

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Abstract

The molecular organization of monolayers at the air–water interface of an amphiphilic azo-phane with unbranched *n*-dodecyl substituents differs from that of the analog with bulky ‘*tert*’-octyl substituents as seen in the area per molecule. Complexation with sodium ions from the aqueous subphase, as deduced from measurement of the surface potential, is facilitated by closer approach of the macrocycles for the *n*-dodecyl-substituted azo-phane, since two macrocycles form the complex with Na⁺. The compensation of the positive charge after complexation in the case of a two-component monolayer of the *n*-dodecyl-substituted azo-phane and octadecanoic acid, molar ratio azo-phane to acid = 2:1, enhances even more the complexation. The complex equilibrium constants and the contributions of the hydrophilic head group region to the surface potential are evaluated from Langmuir isotherm fits to the dependencies of the surface potential on the NaCl concentration in the aqueous subphase for the three monolayer systems investigated, i.e., the two different pure azo-phane monolayers and the two-component monolayer.

Abbreviations: DA3 – 1,5-bis-(2,2'-azo-4,4'-(1,1,3,3-tetramethylbutyl)-)phenoxy)-3-oxapentane; DA6 – 1,5-bis-(2,2'-azo-4,4'-dodecyl)-)phenoxy)-3-oxapentane; ODA – octadecanoic acid

Introduction

Amphiphilic azo-phanes of the type shown in Scheme 1 combine three very valuable properties: (a) selective complexation of alkali metal ions, (b) photo-reactivity and (c) the potential of forming insoluble monolayers at the gas–water interface. In particular, 13-azocrown derivatives have received much attention recently [1–5]. Further, the monolayers may be transferred to solid substrates [6–8] with the option to assemble systems of well-defined architecture for special purposes. The organization of such multifunctionalized molecules in monolayers at the gas–water interface enables one to control or at least to modify the interactions with alkali ions in the aqueous phase. This may be investigated by measuring the surface potential ΔV of the monolayers since the binding of a cation by azo-phane molecules results in the formation of a positively charged head group with the counter ion in the electric double layer underneath. Consequently, the surface potential should increase. This has indeed been observed in the case of the amphiphilic azo-phane DA3 (see Scheme 1), with bulky hydrophobic

substituents (R = 1,1,3,3-tetramethyl-butyl) as shown in Figure 1, reproduced from Ref. [9] Since Na⁺ ions are selectively bound [10], the dependence of the surface potential on the concentration of NaCl in the subphase may be studied, keeping the ionic strength constant by addition of KCl. Binding of Na⁺ ions occurs with the azo-phane in the *E*-configuration only. Therefore, the cation is released upon reversible photo-isomerization of the azo-phane to the *Z*-configuration with consequent variation of ΔV depending on the concentration of NaCl in the subphase [9]. Since two molecules of the azo-phane are required for the formation of the complex, binding of Na⁺ should depend on the approach of the azo-phane rings to each other in the monolayer. Replacement of the bulky hydrocarbon substituents by unbranched chains (e.g., R = *n*-dodecyl, DA6, see Scheme 1) may facilitate this approach, and such an azo-phane is expected to exhibit enhanced binding of Na⁺ as compared to DA3. Further, the incorporation of the cation might be additionally facilitated in a two-component monolayer of amphiphilic azo-phane and long chain fatty acid like octadecanoic acid (ODA) in the molar ratio azo-phane:acid = 2:1 where the carboxylate anion acts as counter ion of the cation after binding Na⁺. We have

* Author for correspondence. E-mail: biernat@chem.pg.gda.pl

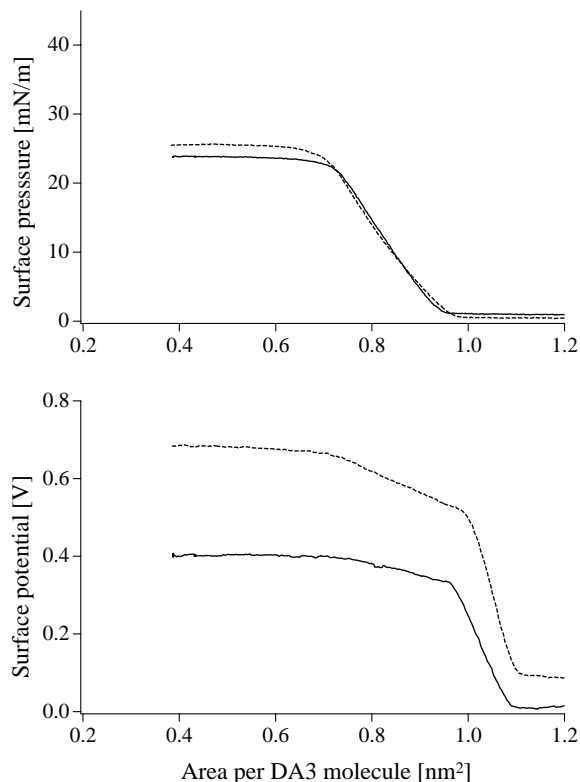
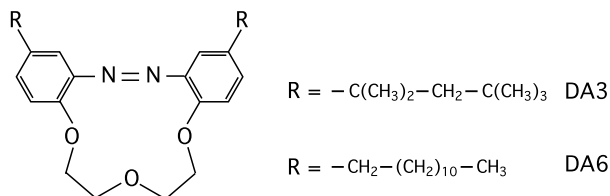


Figure 1. Surface pressure–area (top) and surface potential–area (bottom) isotherms of monolayers of the azo-phane DA3 measured on water (full lines) and 0.1 M NaCl (dashed lines), respectively; 20 °C (data taken from Huesmann et al. [9]).



Scheme 1. Chemical structures of the azo-phanes DA3 and DA6.

investigated the behavior of such monolayers in comparison to that of DA3 described in the literature.

Experimental

Materials

The azo-phane DA6 was synthesized and purified as described earlier [10]. Octadecanoic acid was purchased from Merck (purity > 99%) and recrystallized from methanol. The salts NaCl and KCl (suprapure) were purchased from Merck (Germany). The solvent chloroform (99.8%), HPLC grade, was purchased from Baker Chemicals (Germany). The water (resistivity 18 M Ω cm) was purified in a Milli-Q filtration unit from Millipore Corp.

Methods

Surface pressure–area and surface potential–area isotherms were measured in a rectangular trough made from polytetrafluoroethylene with the dimensions 36 cm (length), 11 cm (width) and 1 cm (depth). The trough was thermostated at 20 °C and enclosed in a box. A Wilhelmy balance provided with a 15 mm wide filter paper as plate was used for the measurement of the surface pressure. The surface potential was measured with a vibrating plate condenser of the type described earlier [11]. As counter electrode, a quadratic Pt plate of 3 cm length was placed at the bottom of the trough. Volumes of 30–40 μ L of spreading solutions of ca. 1 mM concentration were delivered to the initial surface of 363 cm², and after about 10 min of relaxation, the monolayers were compressed at an average speed of 16.2 cm² min⁻¹.

Results and discussion

Monolayers of the azo-phane DA6, either pure or mixed with octadecanoic acid (ODA), molar ratio DA6:ODA = 2:1, were investigated by measuring surface pressure–area (π - A) and surface potential–area (ΔV - A) isotherms. Direct observation of the monolayers by Brewster angle microscopy in order to detect possible formation of an ordered phase of the hydrocarbon chains [12, 13], e.g., in the two-component monolayer, has been impossible presumably due to the small thickness of the hydrophobic part. Therefore, we base our conclusions here on the measured isotherms.

Monolayers of 1,5-bis-(2,2'-azo-4,4'-dodecyl-)-phenoxy)-3-oxapentane (13-AP-3), DA6

Figure 2 shows the (π - A) (top) and (ΔV - A) (bottom) isotherms of DA6 on water (full lines), on aqueous 0.1 M NaCl (dashed lines) and on aqueous 0.1 M KCl (dotted lines). In the case of water, the surface pressure starts rising upon compression at an area per macrocycle of $A_m = 0.69$ nm², as compared to $A_m = 0.96$ nm² in the case of DA3 (see Figure 1). Obviously, the bulky 'tert'-octyl substituents determine the area per molecule in this case. Further, a discontinuity typical for a phase transition is seen at $A_m = 0.59$ nm² with a subsequent steep rise to about $\pi = 30$ mN/m ($A_m = 0.46$ nm²) where a second phase transition seems to occur. These particular features of the π - A isotherm are not observed in the case of DA3 (see Figure 1). We tentatively ascribe the discontinuities in the π - A isotherm to reorientation of the macrocycle that is not seen for DA3 since in that case the bulky hydrophobic substituents prevent close approach of the macrocycles.

The π - A isotherm in the presence of 0.1 M KCl in the aqueous subphase (Figure 2 top, dotted line) is very similar to that measured on water, however, shifted to

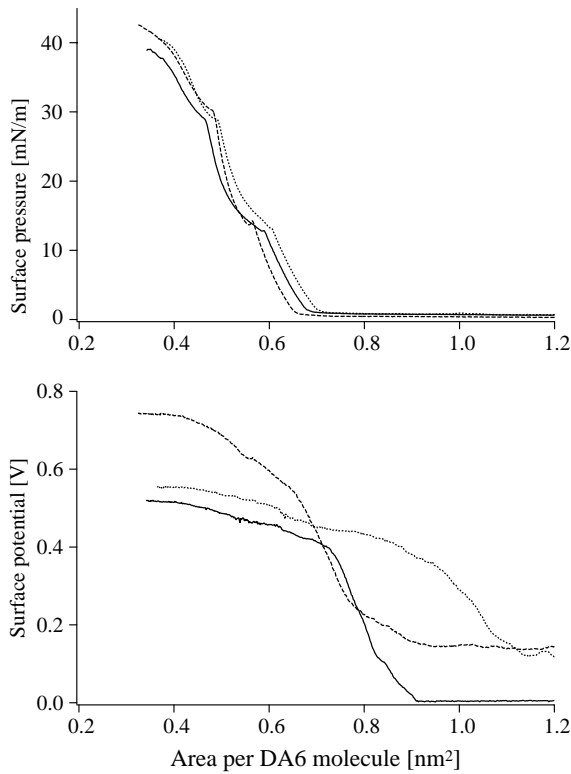


Figure 2. Surface pressure area (top) and surface potential-area (bottom) isotherms of monolayers of the azo-phane DA6 measured on water (full lines), 0.1 M KCl (dotted lines), and 0.1 M NaCl (dashed lines), respectively; 20 °C.

somewhat larger area. Here, the onset of the surface pressure occurs at $A_m = 0.71 \text{ nm}^2$. On 0.1 M aqueous NaCl (Figure 2, top, dashed line), the π - A isotherm is again quite similar to that on water, except that it is shifted to smaller area per molecule with the onset of π at $A_m = 0.66 \text{ nm}^2$. This may be due to the formation of the Na^+ complex of DA6 forcing two molecules of DA6 in close approach.

The ΔV - A isotherms of DA6 on the different subphases shown in Figure 2, bottom, differ considerably for large areas, i.e. for $0.75 \text{ nm}^2 < A_m < 1.2 \text{ nm}^2$. However, in this range, the surface pressure is $\pi \approx 0$, and therefore domains floating around may determine ΔV . In the range between $A_m = 0.70 \text{ nm}^2$ and the second discontinuity in the π - A isotherm (around $A_m = 0.46 \text{ nm}^2$), the ΔV - A isotherms are well reproducible. For water as subphase (Figure 2, bottom, full curve), the lowest values of the surface potential are observed, on 0.1 M KCl (Figure 2, bottom, dotted line) slightly more positive ΔV is measured. As in the case of DA3 (see Figure 1), a strong increase of the surface potential is seen for 0.1 M NaCl (Figure 2 bottom, dashed line) that is related to complexation of the macrocycle.

The surface potential depends on the concentration of NaCl. The values of ΔV at the surface pressure of $\pi = 20 \text{ mN/m}$ observed with monolayers of DA6 at

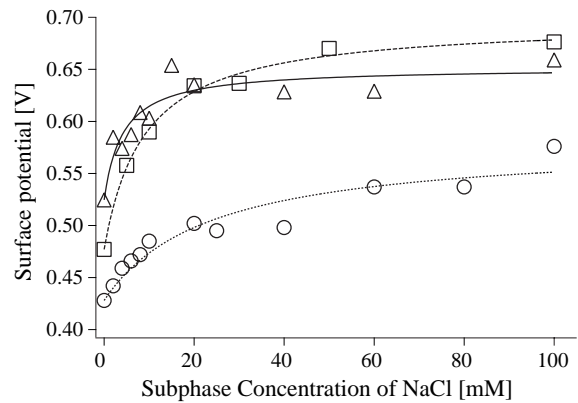


Figure 3. Surface potential of azo-phane monolayers plotted versus concentration of NaCl in the aqueous subphase; circles and dotted line: DA3, surface pressure $\pi = 20 \text{ mN/m}$; squares and dashed line: DA6, $\pi = 20 \text{ mN/m}$; triangles and full line: DA6:ODA = 2:1, $\pi = 25 \text{ mN/m}$; ionic strength in the subphase kept constant by appropriate addition of KCl; lines are least-squares fits to the Langmuir isotherm, Equation (1) 20 °C.

different subphase concentrations of NaCl keeping the ionic strength constant by addition of KCl are represented in Figure 3 as squares. For comparison, the data for DA3 (taken from [9]) are also shown as circles. The values of ΔV for DA6 clearly are more positive than those for DA3. The concentration dependence may be described by a Langmuir isotherm with the adjustable parameters w_0 and w_1

$$\Delta V = \Delta V_0 + c_{\text{NaCl}} / (w_0 + w_1 \cdot c_{\text{NaCl}}), \quad (1)$$

where ΔV_0 is the surface potential at the subphase concentration of NaCl, $c_{\text{NaCl}} = 0$. The least squares fits are represented in Figure 3 as dotted line (DA3) and dashed line (DA6).

We describe complexation of the macrocycle as E isomer by the equilibrium $2E + \text{Na}^+ \rightleftharpoons C$ with the complex constant $K_C = k_{\text{bind}}/k_{\text{diss}}$. The values of the complex constant K_C and of the surface potential at total complexation, ΔV_∞ , are calculated from the adjusted parameters according to

$$K_C = k_{\text{bind}}/k_{\text{diss}} = w_1/w_0; \quad \Delta V_\infty = \Delta V_0 + 1/w_1 \quad (2)$$

and the values using the fits shown in Figure 3 are listed in Table 1. It is obvious that the complex constant in the case of DA6 is larger by about a factor of 3 than in the case of DA3. This is attributed to the particular organization of the macrocycles that is more favorable for complexation in the case of DA6 than DA3.

From the value of the surface potential at total complexation, ΔV_∞ , the contribution of the head group region to the surface potential and consequently the normal component of the dipole moment of the complex may be determined. Different dipoles contribute to the measured surface potential in the absence of NaCl (i.e., on 0.1 M KCl subphase):

Table 1. Parameters of the investigated monolayers of azo-phanes DA3 and DA6, as well as the two-component monolayer DA6:octadecanoic acid (ODA), molar ratio 2:1; quantities ΔV_∞ , K_C and μ_C as evaluated from Langmuir isotherm fits (see lines in Figure 3 and text)

Monolayer	π (mN/m)	A_m (nm ²)	ΔV_0 (V)	ΔV_∞ (V)	K_C (L/mol)	μ_C (D)
DA3	20	0.76	0.428	0.580	43	0.61
DA6	20	0.525	0.477	0.696	138	0.61
DA6:ODA 2:1	25	0.63	0.528	0.652	257	0.41

$$\varepsilon_0 A_m \Delta V_0 = f_Z \mu_Z + f_E \mu_E + \mu_{\text{end}}, \quad (3)$$

where f_Z and f_E are the molar fractions and μ_Z and μ_E the normal components of the effective dipole moments of the hydrophilic moiety of the *Z* and *E* isomer, respectively. The dipole moment μ_{end} is the contribution of the hydrophobic end groups of the whole molecule to ΔV , ε_0 the permittivity of the vacuum and A_m the area per macrocycle. With the surface potential ΔV_∞ in the case of total complexation of the *E* isomer in the monolayer we obtain

$$\varepsilon_0 A_m \Delta V_\infty = f_Z \mu_Z + 0.5 f_E \mu_C + \mu_{\text{end}}. \quad (4)$$

Here, μ_C is the dipole moment contribution of the hydrophilic part of the complex. Assuming that $\mu_E = 0$ (reasonable for azobenzene in the *trans* form) and $f_E = 1$ (thermodynamically more stable isomer, solution kept in the dark for several days) the value of μ_C is obtained according to

$$\varepsilon_0 A_m (\Delta V_\infty - \Delta V_0) = 0.5 \mu_C. \quad (5)$$

The values of μ_C determined in this way are listed in Table 1. It is amazing that the values are identical in the cases of DA3 and DA6, supporting this type of analysis. Further, the value of $\mu_{\text{end}} = 0.67\text{D}$ for DA6 is quite reasonable for two end groups as compared to the value 0.35D per methyl end group in dense-packed monolayers of octadecanoic acid [14]. The larger value obtained in the case of DA3, $\mu_{\text{end}} = 0.87\text{D}$, might be due to contributions of the methyl side groups of the ‘*tert*’-octyl substituents.

Two-component monolayers of DA6 and octadecanoic acid

The area per DA6 molecule at $\pi = 20$ mN/m, $A_m = 0.525$ nm², is larger than the area required by the two long hydrocarbon chains, e.g., $A_{\text{chain}} \approx 0.20$ nm² per chain for dense-packed fatty acid monolayers. It is conceivable, that a molecule of octadecanoic acid may not interfere strongly with a packing of the macrocycles favorable for complexation if it is placed on top of the macrocycles since the area required by two macrocycles is 1.05 nm² and that of five hydrocarbon chains ≈ 1.00 nm². Such an organization should have the advantage of charge neutralization upon complexation thereby enhancing the rate constant of binding, k_{bind} , and reducing the rate constant of dissociation,

k_{diss} . Consequently, we expect a larger value of K_C in the case of a two-component monolayer of DA6 and ODA in a molar ratio DA6:ODA = 2:1 of the particular molecular organization indicated above as compared to that of pure DA6 monolayers.

Figure 4 shows the π - A (top) and ΔV - A (bottom) isotherms of two-component monolayers DA6:ODA = 2:1 on aqueous subphases containing 0.1 M KCl (full lines) and 0.1 M NaCl (dashed lines). The onset of the surface pressure upon compression on 0.1 M KCl is observed at $A_m = 0.88$ nm², i.e., at larger area than for pure DA6 monolayers (0.71 nm²). This is due to the additional area requirement of the ODA molecule per two molecules of DA6. As in the case of pure DA6 monolayers, the isotherm is shifted to smaller area per DA6 on the aqueous 0.1 M NaCl subphase, and the area at 25 mN/m is $A_m = 0.63$ nm² as compared to 0.67 nm² on 0.1 M KCl. Even in the presence of one ODA molecule per two DA6 the area per macrocycle at $\pi = 25$ mN/m is smaller than in the case of DA3

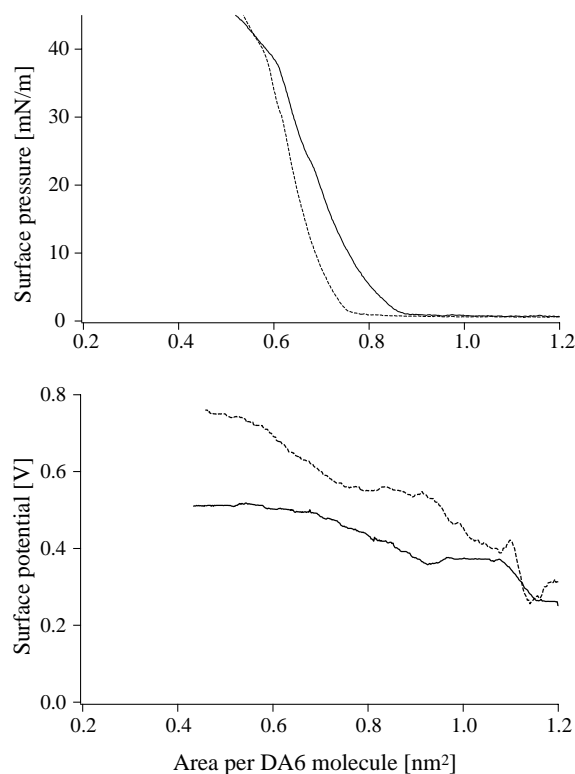


Figure 4. Surface pressure–area (top) and surface potential–area (bottom) isotherms of the two-component monolayer of the azo-phant DA6 and octadecanoic acid, molar ratio 2:1, measured on 0.1 M KCl (full lines) and 0.1 M NaCl (dashed lines), respectively; 20 °C.

($A_m = 0.76 \text{ nm}^2$), and already this fact should give rise to an enhanced value of K_C in case of DA6:ODA = 2:1 as compared to DA3.

The surface potential-area isotherms show a behavior of the two-component monolayer similar to that of pure DA6 monolayers with an increased ΔV in the presence of 0.1 M NaCl (Figure 4, bottom, dashed line) as compared to 0.1 M KCl (Figure 4, bottom, full line) in the subphase. The dependence of ΔV at $\pi = 25 \text{ mN/m}$ on the concentration of NaCl, keeping the ionic strength constant by addition of KCl, is presented in Figure 3, triangles. The full line in Figure 3 is the least squares fit of these data to a Langmuir isotherm. The values of $\Delta V_\infty = 0.652 \text{ V}$, $K_C = 2571/\text{mol}$, and $\mu_C = 0.41\text{D}$ evaluated from the fit parameters w_1 and w_2 are listed in Table 1. The constant K_C is larger by nearly a factor of 2 for the two-component monolayer as compared to the pure DA6 monolayer.

These data clearly indicate that the equilibrium constant K_C is increasing in the series DA3 < DA6 < DA6:ODA = 2:1. This has to be attributed to the molecular organization of the monolayers with the additional effect of charge compensation in the case of the two-component monolayer. A location of the carboxylate group on top of the two macrocycles as assumed above is supported by the reduced value of the dipole moment $\mu_C = 0.41\text{D}$ per macrocycle as compared to $\mu_C = 0.61\text{D}$ in the case of pure DA6. The ratio of DA6:ODA = 2:1 is a consequence of the stoichiometry of the complex, i.e. DA6:Na⁺ = 2:1. The ODA anion therefore can act as a counter ion of the complex according to the stoichiometry. Further, we anticipate a close approach of the $-\text{COO}^-$ group to the cation, since the ODA molecule may fit into the free space between the long chains of the two molecules of DA6 as deduced above from the area requirements. The chloride anion located in the electric double layer may be at larger distance underneath the complex, whereas the $-\text{COO}^-$ group is located above the complex. This should be expressed in the effective dipole moment of the complex.

Conclusion

The organization of the macrocycle in the azophanes DA3 and DA6 is strongly influenced by the hydropho-

phobic substituents, i.e., 'tert'-octyl (DA3) and *n*-dodecyl (DA6) with closer approach of the macrocycles in the case of DA6. Since two macrocycles are required to form the Na⁺ complex, the complex equilibrium constant K_C is larger for DA6 than for DA3 monolayers. An additional enhancement has been achieved in a two-component monolayer of DA6 and octadecanoic acid (ODA), molar ratio 2:1, due to charge compensation after binding the Na⁺ ion. This demonstrates that monolayers may be designed for optimal function.

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