Influence of the counter-anion on the interaction of cations with the benzodithia-18-crown-6 butadienyl dye in monolayers


Abstract

A strong influence of the counter-anions (such as Cl− and ClO4−) on the behavior of monolayers of an amphiphilic benzodithia-18-crown-6 butadienyl dye (dye 1) on aqueous subphases containing alkali metal or heavy metal cations (K+ or Hg2+) is demonstrated for the first time. Deducing from surface pressure–area and surface potential–area isotherms, reflection spectra and Brewster angle microscopy data, dye 1 monolayers show three types of structures depending on the counter-anion’s influence on chromophore association and interactions with heavy and alkali metal cations.

Keywords: Monolayer; Crown-ether; Dye; Ionoselectivity; Photosensitivity

1. Introduction

Structure-functional studies on monolayers of various crown ethers are of permanent interest for scientists working with supramolecular systems [1–4]. Such systems can serve as unique models for fundamental studies of molecular recognition and interaction phenomena at interfaces [2–4]. These systems are also promising for future applications as sensitive components for ion detection in optical and electrochemical devices, as novel membranes for photocontrolled extraction of metal cations, and as materials for recording, storing and processing of optical information [1–4].

During the past years a few studies of photosensitive amphiphilic crown ethers with an azobenzene [5–8] or C=C group [1,4,9–14] as part of the chromophore attached to the macrocycle, have appeared. Our recent studies [9–14] of monolayers and LB films of a series of amphiphilic crown ether styryl dyes with variable size of the polyether ring and varying substitutions in the chromophoric part demonstrated the possibility of preparing photosensitive films with the ability to selectively bind particular alkali and heavy metal cations. Recently, an analogous compound with a butadienyl moiety replacing the styryl moiety in the photosensitive part was synthesized and characterized [15].

The main focus of the previous studies was devoted to the investigation of the cation–ionophore interactions [1,4]. But for a detailed understanding of these phenomena, as well as for further potential applications of such systems, other types of interactions cannot be neglected [2,3]. It is therefore necessary to investigate the influence of the counter-anion that may play a specific role in the interaction between cation and ionophore, as well as between ionophore molecules [2,3]. For example, we found that complex formation between potas-
sium and valinomycin strongly depends on the nature of the counter-anion [16].

In our investigation we compared salts containing chloride, which is the most used and well-studied anion [17–20], with salts containing perchlorate. Perchlorate was chosen because of its presence in the studied butadienyl dye. In addition, the use of perchlorate instead of chloride as counter-anion had a significant influence on the rate of transfer of various alkali metal cations through a bulk liquid membrane containing dibenzo-18-crown-6 [17]. In contrast to chloride, perchlorate anions exhibit a very weak capability to form hydrogen bonds with water molecules [18,19]. Therefore, the perchlorate anion can be considered as a ‘breaking ion’ that destroys the hydrogen bond network between water molecules [18,19]. Also, the perchlorate anion is frequently taking part in coordination with the complexes of crown ethers and cations as observed by infrared spectral changes and proposed as a ‘diagnostic test’ for the coordination of the ethers and cations as observed by infrared spectral changes.

The main aim of this work was to study the influence of the counter-anion’s nature and concentration on the ionselective and photosensitive properties of dye 1 in monolayers.

2. Experimental

2.1. Materials

The amphiphilic benzo-18-crown-6 butadienyl dye (dye 1) was prepared according to the method developed by the authors and described earlier [15].

Dye 1 has previously been thoroughly characterized by elemental analysis, NMR- and IR-spectroscopy [15]. The salts KClO₄ (99+%), KCl (99%), Hg(ClO₄)₂ (98%) and HgCl₂ (98%) were purchased from Aldrich and used without further purification. The water was purified with a Milli-Q filtration unit of Millipore Corp. (specific resistance 18 MΩ cm, surface tension 72.7 mN/m at 20 °C).

2.2. Methods

The surface pressure (π)–molecular area (A) and surface potential (ΔV)–molecular area isotherms of dye monolayers were recorded on a rectangular trough (dimensions 11 cm × 36 cm × 1 cm) made from poly(tetrafluoroethylene) equipped with a 15 mm wide filter paper Wilhelmy balance and vibrating plate condenser (with Pt plate, operating at 400 Hz, 1.5 cm diameter). The 1 mM dye 1 solution (35 μl) in chloroform was spread onto water or various aqueous salt solutions (21 °C), and the monolayers were compressed by moving the barrier with constant speed reducing the surface area by about 16.1 cm²/min.

Dye monolayers were characterized by Brewster angle microscopy (BAM) [22] using a MiniBAM (NFT Göttingen) equipped with a laser diode, emission wavelength 660 nm. Reflection spectra were analyzed by non-linear curve fitting using Origin 6.1. The interval from 375 or 400 to 700 nm was used, to avoid contributions from the small intensity band at about 340–360 nm. It was excluded from the analysis because of excessive noise at short wavelengths and the instrument cut off at 420 nm.

To avoid any possibly photoreactions of dye 1, all experiments were done under the red light.

Reflection spectra were analyzed by non-linear curve fitting using Origin 6.1. The interval from 375 or 400 to 700 nm was used, to avoid contributions from the small intensity band at about 340–360 nm. It was excluded from the analysis because of excessive noise at short wavelengths and the instrument cut off at 300 nm.

3. Results and discussion

3.1. Dye monolayers on aqueous solutions of KClO₄ and KCl

According to the π–A and ΔV–A isotherms (Fig. 1a and b), the behavior of dye 1 monolayers on aqueous solutions of KClO₄ at low concentrations (10⁻⁵ to 10⁻² M) is close to that on water [15]. For example, collapse pressures are in the range from 41 to 45 mM/m at an area of about 0.55–0.50 nm².
The isotherms become quite different at higher KClO₄ concentrations (10⁻⁴ to 10⁻² M). The surface pressure of dye 1 monolayers is much smaller upon compression than on water with values from 18 to 22 mN/m at an area of about 0.60 nm². In addition, the π–A isotherms, upon further compression, show a small increase of the surface pressure after a flat region at areas of 0.35–0.30 nm² and surface pressures of about 30 mN/m. That may be interpreted as ‘broad’ collapse of the dye 1 monolayers. Also, we see a pronounced increase of the surface potential values from 550 to about 750 mV when increasing KClO₄ concentrations (Fig. 1 b). The form of the surface potential isotherms changes from a gradual increase during compression (Fig. 1 b, curve 4), similar to the behavior on water, to an abrupt increase (Fig. 1 b, curves 5 and 6).

When using KCl (Fig. 2 a), isotherms differ little from their behavior on water when concentrations are kept below 10⁻⁴ M. At larger values (10⁻⁴ to 10⁻² M), changes become more pronounced: the area values are higher at low pressures and smaller at high pressures as compared to those on water, whereas the areas of monolayer collapse are almost the same and collapse pressures are decreasing only by about 5 mN/m.

In general, at high KCl concentrations (10⁻⁴ to 10⁻² M) dye 1 monolayers become more expanded as compared to a pure water subphase.

The surface potential values of dye 1 monolayers on KCl containing subphases are higher than those on water [15] and increasing with the KCl concentration (Fig. 2 b). At the same time the character of ΔV = A isotherms preserves the gradual increase. These findings can be explained by the increase of the subphase’s ionic strength.

In order to eliminate effects that are merely due to this change of ionic strength, we then used aqueous subphases with a constant total salt concentration at 1 mM, containing both KCl and KClO₄. Subsequently we varied the fractions of the two salts. A few such isotherms are shown in Fig. 3. There are some differences in the π – A isotherms (Fig. 3a),
Fig. 3. Surface pressure–area isotherms (a) and surface potential–area isotherms (b) of dye 1 monolayers on mixed KClO$_4$ and KCl subphases: 0.01 mM KClO$_4$ and 0.99 mM KCl (curves 1 and 4), 0.07 mM KClO$_4$ and 0.93 mM KCl (curves 2 and 5), 0.50 mM KClO$_4$ and 0.50 mM KCl (curves 3 and 6).

Fig. 4. BAM images (5.134 mm × 6.869 mm) of dye 1 monolayers at 10 mN/m on 1 mM solutions of KCl (a), mixture of 0.11 mM KClO$_4$ and 0.89 mM KCl (b), mixture of 0.5 mM KClO$_4$ and 0.5 mM KCl (c).
which are observed mainly at high surface pressures, since the monolayer collapse occurs at lower surface pressures when increasing the fraction of KClO₄. Differences are more pronounced for shape and values of the $\Delta V - \Delta$ isotherms (Fig. 3b). They change from a gradual increase of surface potential to about $\Delta V = 400$ mV upon compression in the case of 1% of KClO₄ (Fig. 3b, curve 4) to a sharp increase to almost 750 mV in the case of 50% of KClO₄ (Fig. 3b, curve 6). Interestingly, this is similar to the behavior on $10^{-5}$ KClO₄ (Fig. 1b).

Some peculiarities of dye I organization in monolayers at $\pi = 10$ mN/m on the studied subphases are also expressed in the topography as seen by Brewster angle microscopy images (Fig. 4a–c). In 1 mM KCl solution (Fig. 4a) as well as on distilled water [15] there are two different regions in dye I monolayers, one of which (darker) could be described as ‘quasi-homogeneous’. The other exhibits inclusions appearing brighter and indicates the presence of a second species, possibly aggregates. BAM images of the monolayers on mixtures of KCl and KClO₄ exhibit sharp domains (Fig. 4b). Their size and amount increases when increasing KClO₄ fraction (Fig. 4c) and become similar to those on 1 mM KClO₄ solution [15]. The strong contrast in the inhomogeneous regions could be due to different azimuth with respect to the incident p-polarized light.

Further information on the types of dye I monolayer structures, as well as on dye-cation complexation was gained by measuring reflection spectra of the monolayers on distilled water and the various salt solutions. In all cases strong bands are observed in the range of 400–650 nm (Fig. 5). The spectra of dye I monolayers measured at different surface pressures on KCl solution are very similar to those on distilled water, but rather different from those on KClO₄ solutions. Both the shape of the reflection curve (narrow in the case of KCl and broad for KClO₄) and the reflection maximum position (444 nm for KCl and 522–535 nm for KClO₄) differ significantly. To eliminate the effect of ionic strength we measured spectra for the mixtures of the two salts. As expected, in case of a high amount of KCl in the salt mixture (Fig. 5a, curve 1) the spectrum is almost as on pure KCl. All spectra indicate the presence of several species and were analyzed by nonlinear curve fitting of Gauss functions. The results indicate, that three different bands peaking at (1) 437 nm, (2) 465 nm and (3) 558 nm (Fig. 5b) are present, with their relative intensity strongly depending on the fraction of KClO₄ in the salt mixture. The contribution from band (1) is the largest at 0.01 mM concentration of KClO₄ and diminishing when increasing the perchlorate fraction in the subphase. In contrast, the strength of band (2) increases, but then diminishes again for the equimolar mixture. For this mixture the contribution of band (3) is the largest and there is no contribution from band (1). Because the parameters of band (2) are very similar to the absorption spectrum of dye I in acetonitrile solution, we assume that it stems from the monomeric form of dye I. The blue-shifted band (1) may be attributed to the formation of, e.g., head-to-tail dimers of dye I with the cationic heterocycle interacting with the macrocycle of the neighbor molecule, which was recently found in crystals of a dye with a similar structure [24]. The red-shifted peak (3) is possibly due to a particular association of dye I molecules caused by non-specific interaction with the perchlorate-anion (probably, ‘sharp domains’, as seen by BAM, Fig. 4b and c).

### 3.2. Dye monolayers on aqueous solutions of Hg(ClO₄)₂ and HgCl₂

In the case of high concentrations ($10^{-4}$ to $10^{-2}$ M) of Hg(ClO₄)₂, dye I monolayers have two states: a liquid-expanded state between $\pi = 0$ mN/m ($A = 1.2$ nm²) and 10–20 mN/m ($A = 0.9$ nm²) and liquid-condensed state between $\pi = 20$ mN/m ($A = 0.8$ nm²) and 55 mN/m ($A = 0.4$ nm²) with a more ($10^{-4}$ to $10^{-2}$ M) or less ($10^{-5}$ M) pronounced transition in between (Fig. 6a). The significant difference between the $\pi - A$ isotherms on Hg(ClO₄)₂ and those on other salts as well as on water indicates a specific interaction (complex formation) between the ‘macrocycle’ and the Hg²⁺ ion. The enhanced repulsion of the positively charged molecules due to complex formation in this monolayer is a reasonable explanation for the pronounced increase (about 30%) of area per molecule in the liquid-expanded state in the presence of Hg²⁺ as compared to other salts or water. On low concentrations ($10^{-6}$ to $10^{-4}$ M of Hg(ClO₄)₂, dye I monolayers (Fig. 6a) have only one liquid-condensed state, similar to that on the other salt solutions and distilled water. The pronounced increase of the surface potential values when increasing the Hg(ClO₄)₂ concentrations (from $10^{-6}$ to $10^{-3}$ M) (Fig. 6b) is accompanied by a change of character of the surface potential isotherms from an almost gradual
Fig. 6. Surface pressure–area isotherms (a) and surface potential–area isotherms (b) of dye 1 monolayers on aqueous solutions of Hg(ClO$_4$)$_2$ at various concentrations: 10$^{-6}$ M (curves 1 and 4), 10$^{-4}$ M (curves 2 and 5) and 10$^{-2}$ M (curves 3 and 6).

increase (Fig. 1b, curve 4) to a pronounced ‘jump’ (to about 450 mV, Fig. 6b, curve 6).

At low HgCl$_2$ concentrations (10$^{-6}$ to 10$^{-5}$ M) the surface area values are higher at low pressures and smaller at high pressures, as compared to those on water (Fig. 7a). Monolayer collapse occurs at lower surface pressure corresponding the smaller areas. At high HgCl$_2$ concentrations (from 10$^{-4}$ to 10$^{-2}$ M) dye 1 monolayers become more condensed in contrast to the more expanded dye 1 monolayers on the same concentrations of KCl (Fig. 2a and b). A further, small decrease in surface areas and pressures of monolayer collapse was observed in this case (Fig. 7a and b).

Differences in organization of dye 1 in monolayers on HgClO$_4$ versus HgCl$_2$ solutions can also be seen in the topography visualized by BAM images (Fig. 8a and c, respectively). These are more pronounced just after monolayer spreading ($\pi$ = 0.1 mN/m) than in partially compressed monolayers ($\pi$ = 10 mN/m) (Fig. 8a and b). For example, for HgCl$_2$, a variety of bright domains (Fig. 8a) formed by dye 1 molecule self-assembly, immediately after spreading and chloroform evaporation. This effect cannot be observed for dye 1 monolayers on Hg(ClO$_4$)$_2$ (Fig. 8c). During compression of the monolayer to $\pi$ = 10 mN/m, these domains are fusing, forming a continuous film with small defects and barely visible edges between neighboring domains (Fig. 8b). In contrast, on Hg(ClO$_4$)$_2$ almost homogeneous monolayers are formed when increasing surface pressure [15]. The formation of shapeless domains on HgCl$_2$ indicates the presence of large aggregates.

Reflection spectra on Hg(ClO$_4$)$_2$ solutions with concentrations from 5 × 10$^{-5}$ to 5 × 10$^{-4}$ M at low surfaces pressures (up to 10 mN/m) are very similar to those on 1 mM Hg(ClO$_4$)$_2$ [15] and have their maximum at a wave length of 470 nm and a FWHM of about 112 nm (Fig. 9a). Exceptions are the spectra at 10$^{-5}$ and 2 × 10$^{-5}$ M concentration with a much broader, red-shifted band (Fig. 9a and b, curves 1 and 2).
Fig. 8. BAM images (5.134 mm × 6.869 mm) of dye 1 monolayers on 1 mM solution of HgCl$_2$ at surface pressures 0.1 mN/m (a), 10 mN/m (b) and on 1 mM Hg(ClO$_4$)$_2$ at 0.3 mN/m (c).

Fig. 9. Reflection spectra of dye 1 monolayers at surface pressure 1 mN/m (a) and 20 mN/m (b) on Hg(ClO$_4$)$_2$ at various concentrations: $10^{-5}$ M (1), $2 \times 10^{-5}$ M (2), $5 \times 10^{-5}$ M (3), $10^{-4}$ M (4) and $5 \times 10^{-4}$ M (5). Those spectra are very similar to the spectrum on an equimolecular mixture of KC1 and KClO$_4$ (Fig. 5, curve 4). When increasing the surface pressure, pronounced changes are observed for all reflection spectra (Fig. 9b), except the latter two, which remain almost the same. The spectra now have different maxima and shapes depending on salt concentration while peaks are generally blue-shifted for an increase of Hg(ClO$_4$)$_2$ concentration but shift back to longer wavelengths for $5 \times 10^{-4}$ M. Because these changes are observed at high surface pressures, they can probably be ascribed to different reorganization phenomena during monolayer compression. One possible explanation is the presence of aggregates and monomeric dye 1 at $10^{-5}$ and $2 \times 10^{-5}$ M (Fig. 9b, curves 1 and 2), monomeric form and dimers at $5 \times 10^{-5}$ and $10^{-4}$ M (Fig. 9b, curves 3 and 4) and a dominance of monomeric dye 1 at $5 \times 10^{-4}$ M (Fig. 9b, curve 5) and 1 mM Hg(ClO$_4$)$_2$ concentration [15]. Fitting Gauss functions to the spectra indicates the simultaneous presence of at least three bands. Therefore, all three types of the dye 1 monolayer structures can be observed in the monolayers on Hg(ClO$_4$)$_2$ at con-
Fig. 10. Reflection spectra of dye 1 monolayers at surface pressure 10 mN/m on HgCl₂ at various concentrations: 10⁻⁶ M (1), 10⁻⁴ M (2) and 10⁻² M (3).

Fig. 11. Changes of the reflection intensity at 470 nm of dye 1 monolayers upon photoactivation at surface pressure 10 mN/m on the 1 mM solutions of Hg(ClO₄)₂ (1) and HgCl₂ (2). The arrows indicate the times when illumination was switched on (↓) and off (↑).

3.3. Photoisomerization

Dye 1 monolayers on 1 mM HgCl₂, as well as on distilled water and KCl containing aqueous subphase, showed a sharp decrease of the reflection maximum upon illumination. The light was switched off before the reflection intensity could reach a minimum. No (or negligible) increase of ΔR was observed in the dark (Fig. 11, curve 2). In contrast, in the presence of Hg(ClO₄)₂ the photoinduced changes of ΔR are reversible since ΔR increases almost to the initial value after the light has been switched off (Fig. 11, curve 1). Thus, counter-anions can play an important role in complex formation between dye 1 and Hg²⁺ ions.

4. Conclusions

The influence of the counter-anions, such as Cl⁻ and ClO₄⁻, on the structures of amphiphilic benzodithia-18-crown-6 butadienyl dye (dye 1) monolayers on aqueous subphases containing alkali metal or heavy metal cations (K⁺ or Hg²⁺) was analyzed. Deduced from surface pressure–area and surface potential–area isotherms, reflection spectra and Brewster angle microscopy data, the dye 1 monolayers showed three types of structures (dimers, monomers or complexes with cations, and aggregates), depending on chromophore association caused by interactions with heavy and alkali metal ions as well as with the anions. The large variety of monolayer structures is probably due to numerous types of interactions at the interfaces between the functional groups of dye 1 molecules with the mixtures of cations and counter-anions.

When specific interactions between the cation and dye 1 occur, such as the complex formation with Hg²⁺, the influence of the counter-anion on monolayer organization is small. However, it can influence more complex behavior, as seen from the photoisomerization experiments.

When there are no specific interactions of dye 1 with the cation, as in the case of K⁺, interactions with the counter-anion can dominate monolayer organization. In particular, the perchlorate anion causes the aggregation of dye 1, while the chloride anion does not seem to influence it.
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