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Mixed monolayers of a photosensitive crown-ether derivative and a polymer as the prototype of sensing nanomaterials

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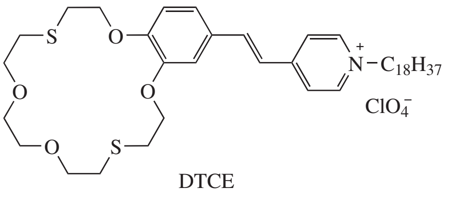
The interaction of a photosensitive and surface-active dithiacrown-ether derivative (in polymer-based mixed monolayers) with Cd^{2+} from aqueous solutions, which has been found by surface pressure, potential and spectral changes, is promising for future applications in nanosized sensing materials.

Heavy metal ions (cadmium, mercury, lead, *etc*.) are hazardous to the environment.[1,2] Therefore, the development of simple and reliable sensors for their detection in aqueous solutions is a problem of considerable current interest. Crown-ether derivatives, which have ion-selective, photosensitive and surface-active properties, can be promising sensor materials selective for guest molecules and ions.[3,4] Previously, we found the selective properties of crown ethers to metal ions,[3,4] in particular styryl and butadienyl thiacrown-ether derivatives can selectively bind metal cations[5,6] and small organic molecules in monolayers at air–water interfaces.[7,8] In contrast, the binding ability of these thiacrown ethers to cations in aqueous solutions is worse than that in organic media.[9–11] However, the detection of heavy metal cations in aqueous solutions is very important for practical applications.[12,13] The arrangement of crown-ether derivatives in insoluble films at organic–water or air–water interfaces gives a good possibility to bind strongly and specifically particular cations from aqueous solutions underneath these interfaces. The properties of multifunctional crown-ether derivatives in organic solutions[14,15] and at the interfaces[16,17] are different. These compounds were characterized by classical and modern methods[18–21] to visualize their interactions with metal cations.

Here, we report the preparation of the mixed monolayers of a recently synthesized photosensitive dithiacrown-ether (DTCE) and polymer derivative for sensing cadmium ions.[†]

The isotherms of surface pressure (π) and surface potential (ΔV) *vs*. area (A) per DTCE molecule in a monolayer were measured using a self-made rectangular trough of polytetrafluoroethylene (PTFE) with the dimensions of 11×38×0.8 cm[19] and a surface pressure sensor based on the Wilhelmy method,[18–21] which provide information on phase separation, molecular packing density at the interface, *etc*.[19,20] The monolayer preparation procedure included (1) the spreading of a precise amount (from 5 to 60 μl) of a DTCE solution or DTCE–PVS mixtures in twice-distilled water (or salt solution); (2) the film relaxation for 10 min in order to evaporate the solvent and to form a monolayer;[19] and (3) continuous compression by moving the barrier with a constant speed of 10 cm^2 min^{-1}. The ΔV–A isotherms of a DTCE monolayer were obtained by a vibrating electrode method, which is based on the measurement of potential difference between a metal electrode disk vibrating at an ultrasonic frequency above the water subphase (several millimeters) and a Pt electrode immersed in an aqueous subphase.[19–21] The experimental errors in π, ΔV and A were ± 0.1 mN m–^{1}, ± 0.003 V and ± 0.05 nm^2 per molecule, respectively.



DTCE

In our first experiments, the DTCE monolayers were obtained by the spreading of a solution of individual DTCE (1.074 mmol in chloroform) on twice-distilled water.[4] A stable surface pressure of about 0.5 mN m^{-1} was observed for spreading 5 μl of DTCE solution, and it became almost constant upon further DTCE monolayer compression in a range of 2–10 nm^2 at the initial section of an isotherm (Figure 1, curve *1*). The formation of a reproducible liquid-expanded (LE) state of DTCE monolayers on water by spreading 25 μl of the above DTCE solution occurred (Figure 1, curve *2*). The collapse pressure of this state I in the individual DTCE monolayers was found at relatively high pressures of 27 mN m^{-1} at 0.45 nm^2 per molecule (Figure 1, curve *2*). The differences between curves *1* and *2* in Figure 1 at about 2 nm^2 are due to different DTCE spreading volumes. A gradual increase in the surface potential [Figure 1(*b*), curve *1*] from –300 to –100 mV was observed upon DTCE monolayer compression in a wide range of surface areas (from 2 to 10 nm^2). This indicates a nearly horizontal position of complicated multifunctional DTCE molecules regarding the interface at the initial time of the experiment (5 min after spreading the solution on twice-distilled water). In contrast, a more rapid increase in the surface potential [Figure 1(*b*), curve *2*] from –60 to 130 mV was detected on further DTCE monolayer compression from 2.0 to 0.45 nm^2. This corresponds to a transition from nearly horizontal to almost vertical positions of DTCE molecules with regard to the interface. A further decline of the potentials at the areas smaller than 0.45 nm^2 is caused by the conditions of monolayer measurements at such small areas in the vicinity of the vibrating electrode

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[†] The synthesis of amphiphilic and photosensitive dithiacrown-ether (DTCE) derivatives was described previously.[14]

Chloroform (Baker, 99.8% purity) was used as a solvent for DTCE. Poly(vinyl stearate) (PVS) (M_w ~ 90 000, GPC), which was used as a surface-active polymer, and cadmium perchlorate (>99% purity) were purchased from Sigma–Aldrich.

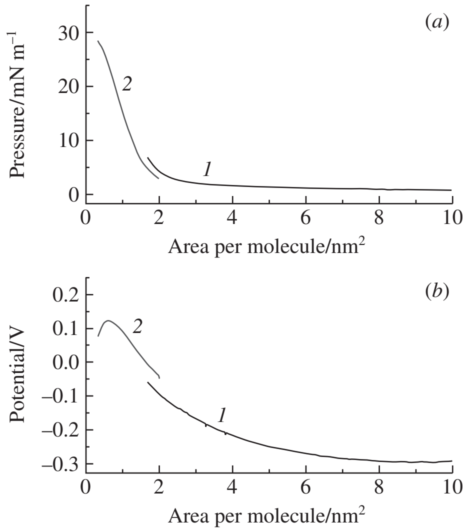

Figure 1 (*a*) Surface pressure and (*b*) surface potential isotherms *vs.* area per molecule in the monolayer of DTCE on a twice-distilled water surface at spreading volumes of (*1*) 5 and (*2*) 25 μl.

(in this region, the potentials did not change even for amounts of DTCE solution of 25–60 μl). Thus, DTCE monolayer organization on water exhibited only an LE state (the close packing of head groups at the interfaces).

We found that a molar ratio of 1:2 for the DTCE–PVS mixtures is the most reliable and suitable according to the mixed monolayer geometry. Two states for such mixed monolayers were observed on distilled water: (I) an LE state at low pressures and (II) a liquid-condensed (LC) state[19–21] at high pressures [Figure 2(*a*)]. These two states demonstrate the contributions of each component in the mixed monolayer: the LE (I) and LC (II) states are mainly due to the presence of DTCE and PVS, respectively. An increase in the cadmium perchlorate concentration from 10^{-7} to 10^{-3} M at the initial moment of DTCE monolayer formation (the area per molecule was about 2 nm^2) led to surface pressures of 0.2–0.3 mN m^{-1} [Figure 2(*a*)]. The monolayer transformed from a LE to a LC state at pressures of 20, 16 and 14 mN m^{-1} (*i.e.*, decreased) and the areas per molecule of 0.9, 0.94 and 1 nm^2 (*i.e.*, slightly increased) at 10^{-7}, 10^{-5} and 10^{-3} M Cd^{2+} concentrations in solutions, respectively. The collapse pressures reached 52.5, 58.0 and 64.7 mN m^{-1} with the same Cd^{2+} concentration increase. Thus, quantitative changes of the surface pressure–area isotherms at different Cd^{2+} concentrations were significant due to interaction of the cadmium cation with DTCE. In contrast, almost no changes were revealed in the surface pressure and potential isotherms for individual PVS monolayers at different concentrations of Cd^{2+} in solutions (see Online Supplementary Materials).

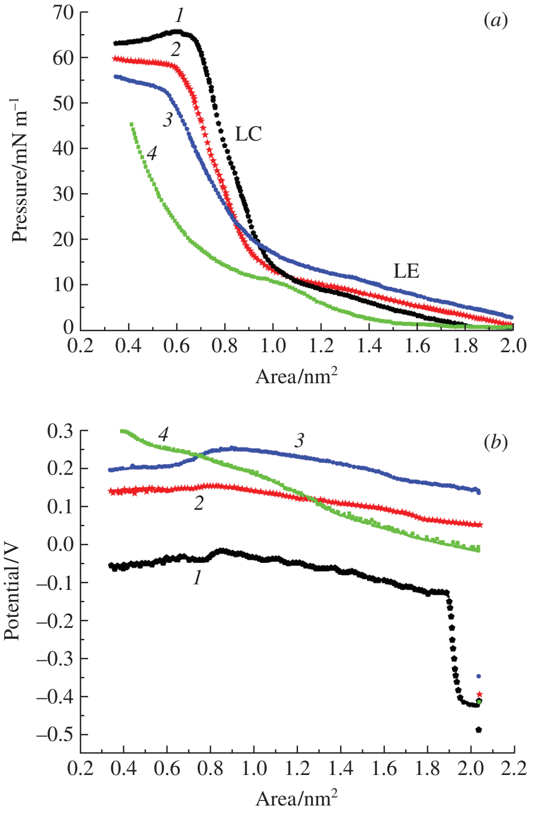

Figure 2 Isotherms of the (*a*) surface pressure and (*b*) surface potential *vs.* molecular area for the DTCE : PVS monolayer on $Cd(ClO_4)_2$ aqueous solution at different concentrations: (*1*) 10^{-3}, (*2*) 10^{-5}, (*3*) 10^{-7} M and (*4*) the same DTCE : PVS monolayer on twice-distilled water at 20 °C.

Qualitative changes in the surface potential isotherms [Figure 2(*b*)] were observed for the mixed monolayers of DTCE–PVS on cadmium perchlorate solutions at concentrations from 10^{-7} to 10^{-3} M. An initial sharp increase (so-called jump) of the potentials occurred at the beginning of monolayer formation at a constant area (*A*) of about 2.0 nm^2 without monolayer compression. This potential jump was characterized by a surface potential change (ΔV) just after DTCE–PVS mixture spreading and film relaxation for 10 min (for solvent evaporation and monolayer formation), which demonstrated values of 488, 445 and 354 mV in the presence of Cd^{2+} at concentrations of 10^{-7}, 10^{-5} and 10^{-3} M, respectively. On a further compression of the mixed monolayer, the ΔV–A isotherm was almost smooth at areas from 2.0 to 0.85 nm^2 (ΔV of 103, 101 and 104 mV) and slightly decreased (ΔV of 39, 15 and 7 mV) at areas from 0.85 to 0.60 nm^2 [Figure 2(*b*)]. These effects can be explained by monolayer collapse in a region from 0.85 to 0.60 nm^2 [Figure 2(*a*)]. The values of ΔV in the mixed monolayer at areas smaller than 0.6 nm^2 were almost constant at all Cd^{2+} concentrations but not on twice-distilled water because the monolayer collapse was not reached in this case [Figure 2(*b*)]. These pronounced differences between Cd^{2+} solutions (at concentrations higher than 10^{-7} M) and twice-distilled water for the same mixed monolayer proved the complex formation between Cd^{2+} and DTCE.

The spectral characteristics of a DTCE monolayer on the aqueous solutions of cadmium cations differed from those on twice-distilled water. The DTCE absorption maximum on a water surface was at 393 nm. In the presence of Cd^{2+}, the absorption maximum shifted by 7 nm (a hypsochromic shift) due to the formation of a cadmium–DTCE complex (see Online Supplementary Materials). For the detection of heavy metals, the DTCE absorption spectra differences are of the same significance as particular changes in their isotherms.[3–5] The experimental data are consistent with those of the interaction between crown-ether derivatives and heavy metal cations such as Cd^{2+}, Zn^{2+},[22] Hg^{2+},[23] Ni^{2+}, Cu^{2+},[24] and Co^{2+}.[25]

Thus, the ultrathin DTCE films stabilized by PVS at a ratio of 1:2 were obtained. Significant changes in the surface pressure and potential *vs.* area at different Cd^{2+} concentrations were found, which resulted from the interaction of the cadmium cation with DTCE. The absorption spectra of DTCE monolayers obtained directly from the water surface or aqueous cadmium perchlorate solutions were analyzed to support such effects. The proposed systems are promising for the fundamental interfacial research (*i.e.* evaluation of the molecular recognition and interaction phenomena of photosensitive ionophores with heavy metal cations *etc.*) and for potential applications (as the prototypes of nanosized sensing materials with optical detection for environmental monitoring).

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.01.016.

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