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Mendeleev Commun., 2010, **20**, 203–204
Mendeleev Communications

Mixed monolayers of a rhodamine derivative

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DOI: 10.1016/j.mencom.2010.06.006

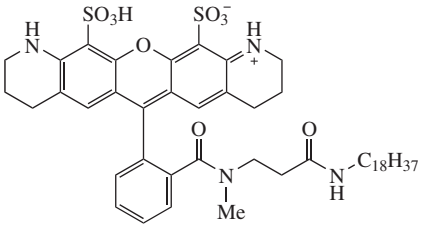
Mixed monolayers of a rhodamine derivative (GM142) with stearic acid were prepared and their surface-active and optical properties were investigated for application in nanophotonics.

The preparation and investigation of dye monolayers with desirable surface-active and optical properties is a rapidly growing research field of both fundamental and applied importance.[1–3] A study of dye–lipid interactions in monolayers can be considered as the simplest model of the first steps of dye inclusion into the plasma membrane and subsequent transport into the cell to mark intracellular objects.[2–4] These molecular interactions in dye–lipid systems are of considerable current interest.[3–5]

The synthesis of photoactivable rhodamine derivatives[6] and studies of their photochromic reactions with the light-induced activation of fluorescence and thermal relaxation to the initial colourless state[7] has triggered efforts for their application in modern confocal microscopy and nanoscopy.[8] Rhodamine derivatives can be spontaneously included in cells and intracellular structures,[9,10] but their interactions with biological membranes or model monolayers have not been studied in detail.

Here, we report the preparation and investigation of the mixed monolayers of a fluorescent rhodamine derivative (GM142) with stearic acid.

For the preparation of monolayers and the measurement of surface pressure – area and surface potential – area isotherms, devices based on the Langmuir principle[4] were used. The mixed monolayers of GM142 with stearic acid at various molar ratios were transferred onto glass plates (38×12 mm) by the Langmuir–Blodgett method[4] at a constant surface pressure of 20 mN m^{-1}. The spectral characteristics of GM142 in solution were studied using Cary 4000 UV-VIS and Cary Eclipse Fluorescence spectrophotometers. For monolayer systems on glass plates, specially made absorption and fluorescence spectrophotometers[11] were used.



GM142

GM142 forms only unstable monolayers with a liquid-expanded state and a collapse pressure of about 10 mN m^{-1} [Figure 1(*a*), curve *1*]. However, it can be stabilized in the mixture with a high excess of stearic acid (C18) [Figure 1(*a*), curves *2–4*]. Since the surface pressure is plotted *vs.* area per matrix (*i.e.*, C18) molecule, the shift to larger areas with respect to the isotherm of C18 has to be ascribed to the area occupied by the dye in the mixed monolayer. Taking into account the mixing

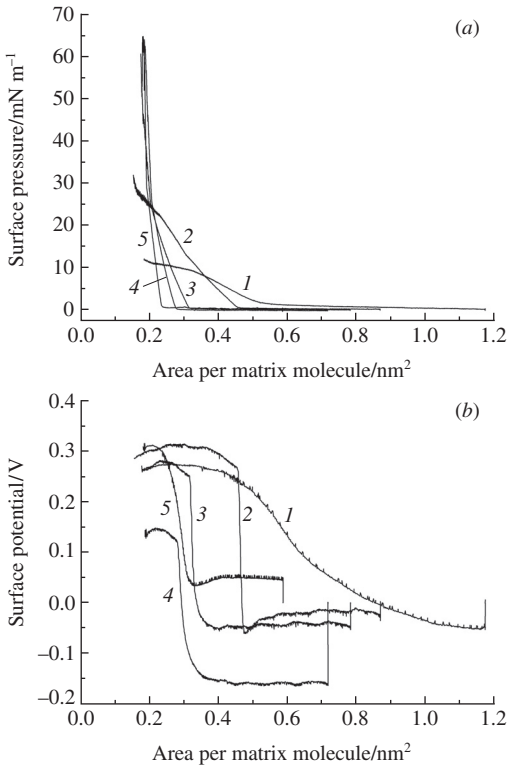


Figure 1 (*a*) Surface pressure *vs.* monolayer area and (*b*) surface potential *vs.* monolayer area for (*1*) pure GM142 monolayer, (*2*) mixed monolayers of GM142:C18 = 1:3, (*3*) GM142:C18 = 1:5, (*4*) GM142:C18 = 1:10 or (*5*) pure stearic acid at the air/water interface.

ratio, the area per dye molecule (not shown here) was estimated at 0.2 nm^2 for surface pressures $\pi \leq 10$ mN m^{-1}. The area of 0.2 nm^2 corresponds to the area occupied by a nearly vertically oriented hydrocarbon chain. This area per dye molecule is reasonable, if the chromophore is covered by C18 molecules with the long chain substituent of the dye packed parallel to the hydrocarbon chains of the matrix.

The surface potential (ΔV) for the mixed GM142:C18 monolayers at the air/water interface jumped down upon spreading (by about 0.05–0.15 V) and remained almost constant during monolayer compression until the surface pressure increases in the area range from 0.44 to 0.28 nm^2 per molecule with a further increase to 0.34–0.30 V [Figure 1(*b*), curves *2–4*]. In contrast, for pure stearic acid monolayers, the surface potential [Figure 1(*b*), curve *5*] increases initially after spreading to 0.05 V and, upon compression, sharply to about 0.26 V. The surface potential of pure GM142 [Figure 1(*b*), curve *1*] decreases initially

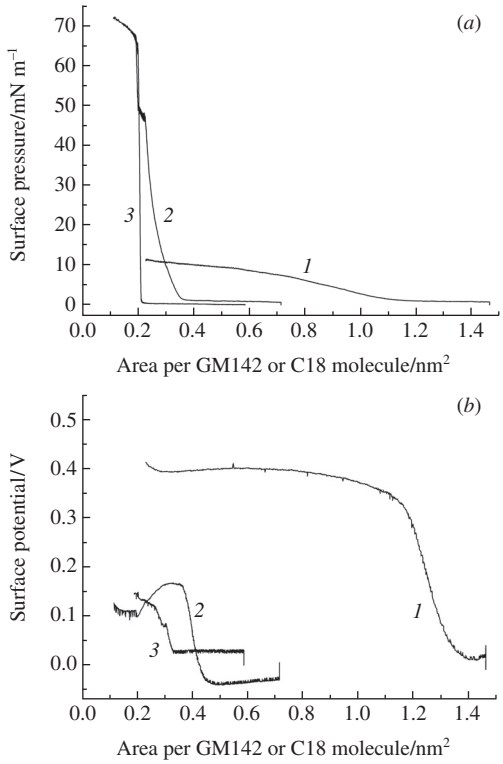


Figure 2 (*a*) Surface pressure *vs.* monolayer area and (*b*) surface potential *vs.* monolayer area for (*1*) pure GM142 monolayer, (*2*) mixed monolayers of GM142:C18 = 1:10 and (*3*) pure stearic acid on an aqueous subphase of 3×10^{-4} M $CdCl_2$ and 5×10^{-5} M $NaHCO_3$.

after spreading to –0.05 V and increases by compression gradually to about 0.27 V in the whole area range (from 1.10 to 0.42 nm^2 per molecule) until monolayer collapse [Figure 1(*b*), curve *1*].

Since monolayers of stearic acid are stabilized by interaction with Cd^{2+} ions in the aqueous subphase, we have chosen this method for GM142. The surface pressure–area isotherm of GM142 on an aqueous subphase of 3×10^{-4} M $CdCl_2$ and 5×10^{-5} M $NaHCO_3$ [Figure 2(*a*), curve *1*] shows no increased stability, as compared to pure water. The main difference is the beginning of surface pressure rise upon compression at around 1.15 nm^2, as compared to 0.55 nm^2 on water. However, the mixed monolayer of GM142:C18 = 1:10 [Figure 2(*a*), curve *2*] clearly indicates a stabilization of GM142. The evaluation of the area per dye molecule (not shown here) yields values ranging from 0.9 nm^2 at 5 mN m^{-1} to 0.22 nm^2 at 25 mN m^{-1}. Therefore, we have selected a surface pressure of 20 mN m^{-1} for the monolayer transfer of GM142:C18 = 1:10 onto glass plates. Initially, the glass plate was covered with a monolayer of C18 (withdrawal), followed by transfer of two monolayers of GM142:C18 = 1:10 (by immersion and withdrawal of the plate).

On the aqueous subphase with $CdCl_2$ and $NaHCO_3$, the surface potential of the GM142 monolayer rises abruptly at about 1.4 nm^2 to values of about 0.35 V and remains nearly constant in the range of 1.0–0.3 nm^2 [Figure 2(*b*)]. Note that the surface potential of GM142:C18 = 1:10, after initial rise is decreasing in the range of 0.28–0.23 nm^2. This may indicate some structural change of the monolayer with C18 molecules occupying the space above the chromophore.

The main spectral characteristics of GM142 in the mixed monolayers with C18 (molar ratio of 1:10) are strong absorption in the range of 480–580 nm with a maximum at 560 nm (Figure 3) and a fluorescence maximum at 575 nm after excitation at 545 nm (not shown). From the spectral data measured under 90° unpolarized (curve *1*), 45° *s*-polarized (curve *2*) and 45° *p*-polarized (curve *3*) incidence, it is possible to determine

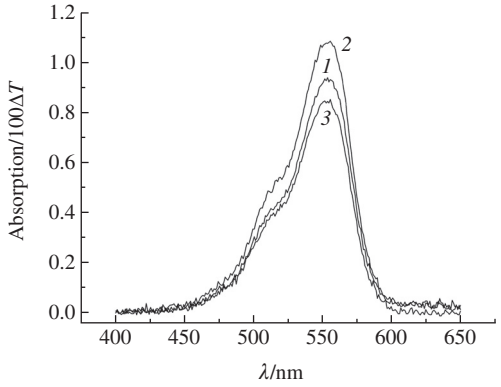


Figure 3. Absorption spectra measured under (*1*) 90° unpolarized, (*2*) 45° *s*-polarized and (*3*) 45° *p*-polarized incidence of the mixed GM142:C18 = = 1:10 monolayer transferred onto glass plates by the Langmuir–Blodgett method.

the chromophore orientation for GM142 in the mixed monolayers with C18.[12] Assuming no preferential orientation of the transition moments in the layer plane, we obtain an angle of 71° with respect to the surface normal. Accordingly, the chromophores are slightly tilted.

Thus, pronounced differences in the stability and organization of GM142 were observed between pure dye monolayers and mixed monolayers with stearic acid at the air–water interface. The above results may be of interest for the modeling of GM142 interactions with cell membranes components.

This work was supported by the Russian Foundation for Basic Research, the Russian Ministry of Science and Education and the Max-Planck-Society (Germany). We are thankful to Lieu Wien (Max-Planck-Institute of Biophysical Chemistry, Germany) and M. N. Shaposhnikov (MSAVM&B, Russia) for their technical assistance.

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Received: 1st March 2010; Com. 10/3476