ESRF	**Experiment title: Cation-Controlled Excimer Packing in Langmuir-Blodgett Films of Hemicyanine Amphiphilic Chromoionophores**	**Experiment number**: SC-4447
Beamline: ID10	**Date of experiment**: from: 10.11.2016 to: 15.11.2016	**Date of report**: 01.03.2017
Shifts: 15	**Local contact(s)**: Oleg Konovalov	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

***Selektor S.L.** [1]

***Shokurov A.V.** [1]

***Raytman O.A.** [1]

***Shcherbina M.A.** [2]

***Bakirov A.V.** [2]

***Buzin A. I.** [2]

[1] **A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS**

[2] **N.S. Enikolopov Institute of Synthetic Polymeric Materials RAS**

Report:

It was revealed that molecules of alkylated aza-di-thia-crown-hemicyanine form on the surface of liquid/air interface monolayers of substantially different structure depending on the composition of the water subphase. It should be noted that no film has shown clear diffraction peaks, thus the conclusions on the structure of the films were made using the method of X-Ray reflectometry.

It was shown that on pure water even at comparatively high surface pressure values (π = 27 mN/m) homogeneous films have not been formed – only very poor oscillations of the intensity at highest pressures were observed, as the roughness of the films was very high.

In contrast, monolayers formed on the subphase containing 1mM of $BaClO_4$ exhibited well-organized structure. The film thickness amounted to circa 27 Å, and already at surface pressure of 10 mN/m the formation of bimodal structure of sublayers with substantially different densities was observed. We suppose that the lower one is organized by crown-ether groups, while the higher one – by aliphatic tails. At the same time the absence of chemical interaction between crown-hemicyanine and Ba is evident from UV-Vis spectra (Fig. 1 curve 2). Both these observations confirm the preorganizing effect of barium cations on the structure of the studied monolayers.

Further experiments on mercury-containing subphases were complicated due to the problems with the supply of mercury perchlorate at chemical lab at ESRF (the whole batch supplied by Sigma-Aldrich was spoiled/contaminated, another was ordered urgently and was out of use as well), we could not prepare solutions with precise concentrations. However, using the spectral data previously obtained by us for studied compound monolayers on subphases containing known concentrations of mercury, we managed to roughly estimate the solution concentrations for reported experiments (SC-4447).

We have found that highly regular monolayers formed on the surface of ~1 mM and ~0.25 mM $HgClO_4$ solutions. Their thickness was calculated to be 22.8 Å, 31.7 Å, and 43.4 Å at 10, 16 and 25 mN/m correspondingly. Moreover, as the distribution of electron density along the normal to the layer is uniform at lower pressures, at 25 mN/m one can see the formation of bimodal structure of sublayers with substantially different densities. We suppose that in this case the lower one is organized by crown-ether groups coordinated by mercury cations. Cation binding is in this case confirmed by UV-Vis spectra recorded *in situ* (Fig. 1b, curve 3).

The most interesting effects were observed in two-stage experiments, in which the solution of mercury salt was added under preliminary compressed monolayer (10 mN/m) into the subphase, already containing barium cations (Fig. 1, curves 4-5). One can see that in this case structure of the film changed substantially after the addition of mercury perchlorate. The process of ordering, though, is rather slow – the layer formed immediately after the addition of mercury, continued to thicken after at least 10 min between two reflectivity measurements. It is especially important in comparison with the same experiment without barium cations. In this case, the addition of mercury perchlorate did not cause such significant changes in film structure that indicate the very pure mercury cation binding in the absence of Ba cations. The difference in the efficiency of cation binding in these two cases was also demonstrated by *in situ* UV-Vis spectroscopy (Fig. 1b, curves 4-5).

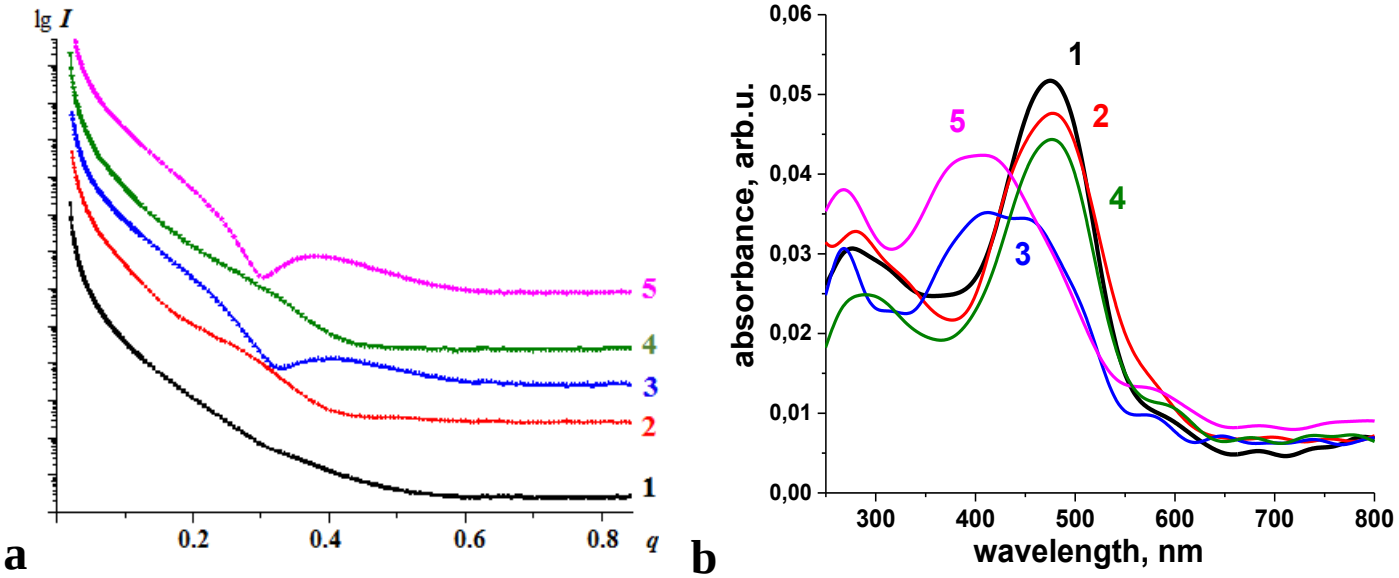

Figure 1. (a) Series of reflectometry curves for Langmuir monolayers of the studied alkylated di-thia-aza-crown-hemicyanine dye and (b) their UV-vis absorbance spectra at surface pressure of 10 mN/m on the surface of (1) pure water, (2) 1mM barium perchlorate solution, and (3) ~0.25 mM mercury perchlorate solution; and after introduction of ~0.25 mM of mercury under preliminary compressed monolayer (10 mN/m) into (4) pure water and (5) barium-containing subphases.