Spectral studies of the dithiacrown ether derivative in the presence of metal cations and modeling their possible complexes

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Abstract

© ISUCT Publishing. The preparation of compositions comprising multifunctional compound is one of the key directions for design of chemosensing materials that are important for the determination of particular ions in solutions. These compounds are characterized by ionophoric and photosensitive parts with reliable optical response and ion-selectivity. Their structures suggest the possibility of the complex formation with particular metal cations. The main goals of this study are as following: a) to investigate the absorption spectra of the novel derivative of the dithiacrown ethers (DTCE), synthesized in the laboratory of Professor S.P. Gromov (Photochemistry Center RAS), both: in salt solutions and in monolayers; b) to study the DTCE interaction with various metal cations, including mercury, as well as to carry out quantum-chemical calculations of their possible complexes. Spectral characteristics were examined in the DTCE acetonitrile solutions and their changes in the presence of some cations were found. The pronounced changes were obtained in the case of Hg^{2+} which are expressed as a hypsochromic shift on 22 nm. Absorption spectra of aqueous solutions of DTCE and perchlorates of alkali, alkaline earth, and heavy metals (lithium, sodium, potassium, cesium, magnesium, calcium, strontium, barium, copper, zinc, lead, cadmium, and mercury) at various concentrations were obtained. When the DTCE concentration equals to 10–5 M, the absorption intensity is low, and DTCE absorption maximum shifts in the presence of all the salts are rather small. The greatest shift (by 6 nm) of the DTCE absorption maximum to shorter wavelengths was observed for the mercury(II) perchlorate only. In order to select the DTCE concentration for further research the spectral dependence of the optical density vs. DTCE concentration was obtained (10 M was the most appropriate value of the DTCE concentration). Based on these results the DTCE extinction coefficient in aqueous solutions was determined ($\varepsilon = 9329$ M–1cm–1). Assuming the formation of the DTCE-cation complexes as 1:1, the metal perchlorates with lack and excess of the cations in the aqueous solutions were chosen. The absorption spectra had minor differences at DTCE concentration of 10–4 M and metal perchlorates concentration of 10–5 M (lack of the metal cations). Maximum hypsochromic shift by 4 nm was observed in the presence of mercury(II) perchlorate. It appeared that the lack of concentration of the metal salt does not allow the formation of complexes between the crown ether ring and a cation. The absorption intensity in the presence of most of salts was slightly reduced up to 85–95 % from baseline. The absorption spectra showed significant shifts of the absorption maxima to shorter wavelengths by 29 nm only in the presence of mercury(II) perchlorate at high concentrations (10–3 M). This fact proves a DTCE selectivity for mercury(II) cation. Moreover, the value of the shift depends on the salt concentration. An additional confirmation of these results was obtained in the study of the absorption spectra of the DTCE monolayers transferred from bidistilled water and aqueous

solutions of Hg(ClO4)2 at constant surface pressure (about 10 mN/m). In all cases, the broad absorption maxima in the region of 350–450 nm were found. The main feature was that the maximum absorption for DTCE monolayer transferred to 10–5 M solution of Hg(ClO4)2 was 0.00575 a.u. at 406 nm. This is by 209% higher than those for the DTCE monolayer transferred from the water. Thus, the shift of the absorption maximum of DTCE monolayer in the presence of mercury salt was 23 nm to shorter wavelengths. This is further evidence of complex formation between DTCE (in monolayer) and mercury(II) cations from the aqueous subphase. For visualization and confirmation of the possibility of complex formation between DTCE and mercury(II) cation the quantum-chemical calculations of their structural models were carried out. The total energy of the optimized structure of the complex between DTCE cation and mercury(II) (with 2 perchlorate counter-anions) is set to E_0 = –565.1231 a.u. It can be compared with the energies of individual species: the DTCE cation (E_0 = –250.5477 a.u.) and Hg(ClO4)2 (E_0 = –314.4877 a.u.). Thus, the change in energy (ΔE) upon complex formation is about –0.0877 a.u. (–230 kJ/mol). High energy of complex formation and high covalency of the Hg–S bonds explain the significant blue shift of the maximum in the absorption spectra of the solutions of DTCE with Hg(ClO4)2.

Keywords