МАТЕРІАЛИ ДЛЯ СЕНСОРІВ

SENSOR MATERIALS

THIN FILMS OF TRET-BUTYL CALIXARENE AS SENSITIVE MATERIALS FOR ORGANIC COMPOUND DETECTORS

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THIN FILM OF TRET-BYTYLCALIX[N]ARENES AS SENSITIVE MATERIALS FOR GAS SENSORS TO THE ORGANIC CHEMICAL COMPOUNDS

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Abstract. Adsorption properties of thin nanostructured films of tret-bytylcalix[n]arenes (n=3, 4, 5, 6, 8) with thickness of about 200 nm to vapors of different organic solvents are investigated. Two methods were used for adsorption measurements — mass-sensitive quartz microbalance and interference colorimetry. Gas sensitive, selective and regenerative parameters of the used calixarene films as sensitive materials for chemical sensors were investigated. It is shown that the calix[5]arene films are most sensitive for detection of chlorine organic compounds. The comparative analysis of responses of quartz microbalance and optical sensor elements for each of the explored sensitive films have been carried out.

Keywords: QCM sensors, RGB-colorimetry, calix[n]arenes

ТОНКІ ПЛІВКИ ТРЕТ-БУТИЛ КАЛІКСАРЕНІВ ЯК ЧУТЛИВІ МАТЕРІАЛИ ДЛЯ СЕНСОРІВ ДО ОРГАНІЧНИХ СПОЛУК

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Анотація. Досліджені адсорбційні характеристики тонких наноструктурованих плівок трет-бутилкалікс[n]аренів (n=3, 4, 5, 6, 8) товщиною близько 200 нм до парів різноманітних органічних речовин. Вимірювання адсорбції каліксаренових шарів проведено двома способами — за допомогою мас-чутливого кварцового мікробалансу та шляхом інтерференційних колориметричних вимірювань. Визначено газочутливі, селективні та регенеративні параметри досліджених плівок як чутливих матеріалів для хімічних сенсорів. Показано, що для детектування хлорвмісних сполук найбільш чутливими є шари на основі каліксарену С[5]А. Проведено порівняльний аналіз відгуків кварцових кристалічних та оптичних сенсорних елементів для кожної із досліджених чутливих плівок.

Ключові слова: QCM сенсор, RGB-колориметрія, калікс[n]арени

ТОНКИЕ ПЛЕНКИ ТРЕТ-БУТИЛ КАЛИКСАРЕНОВ КАК ЧУВСТВИТЕЛЬНЫЕ МАТЕРИАЛЫ ДЛЯ СЕНСОРОВ К ОРГАНИЧЕСКИМ ВЕЩЕСТВАМ

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Аннотация. Исследованы адсорбционные характеристики тонких наноструктурированных пленок трет-бутилкаликс[n]аренов (n=3, 4, 5, 6, 8) толщиной около 200 нм к парам различных органических веществ. Измерения адсорбции каликсареновых слоев проводились двумя методами — с помощью масс-чувствительного кварцевого микробаланса и путем интерференционных колориметрических измерений. Определены газочувствительные, селективные и регенеративные параметры исследуемых пленок как чувствительных материалов для химических сенсоров. Показано, что для детектирования хлорсодержащих соединений наиболее чувствительными являются слои на основе каликсарена C[5]A. Проведен сравнительный анализ откликов кварцевых кристаллических и оптических сенсорных элементов для каждой из исследованных чувствительных пленок.

Ключевые слова: QCM сенсор, RGB-колориметрия, каликс[n]арены

Introduction

Chemical sensors are the rapidly evolving fields of the modern sensor science. Majority of investigations in this area is concentrated towards diminishing the sensor overall dimensions, achieving higher sensitivity and lower reaction times, and also search for new highly selective materials for various analytes detection. Chemical sensors are widely applied in medical diagnostics [1] and biomedical analysis [2, 3], in environmental monitoring (continuous and long-term monitoring of detrimental compounds) [4, 5], in food industry [6-8] and pharmacology [9-11], cosmetics production etc.

The necessity of characterization and identification of multicomponent mixtures has lead to development of the multisensor arrays. The question of sensitive layers selectivity to specific gaseous mixtures is essential for creation of intelligent systems for taste and odor discrimination based on such sensors.

Taking into account the ability of organic materials to form various types of molecular interactions and their variety, the organic sensitive layers are most attractive as to their use in the new generation of sensor arrays. Ability of volatile compounds to be adsorbed into molecular capsules of different forms and sizes provides the increased selectivity, good affinity and high sensitivity of such layers toward analytes. These properties are well pronounced in the volumetrically porous organic materials consisting of the complex multiatom molecules (macrocycles, calixarenes, polymers) which are able to bind various organic substances and gases due to the presence of molecular cavities.

Use of the molecular organic crystals opens wide possibilities for formation of sensitive architectures with predefined chemical functionality. Characteristic examples of this approach are given by the use of various cavitands, first of all calixarenes [12-14], which are very promising materials considering the possibility of optimization of their structure to match the analyte molecules' one [15-20]. These peculiarities of the molecular structure (presence of the nanocavities) and also the ability of molecular recognition of the organic compounds allow to utilize the calixarenes for creation of the gas sensors sensitive layers [21].

The aim of the present work is investigation of the sensitivity and selectivity of sensitive layers formed with thin films of tret-butylcalixarenes in chemical and gas sensors for detection of various organic substances, and also conduction of the comparative analysis of responses of the quartz crystal and optical sensor elements as related to correlation between the adsorbed molecular mass and corresponding change in optical parameters for each of the sensitive films under consideration.

Materials and methods

In this work thin films of C[3]A, C[4]A, C[5]A, C[6]A, C[8]A tret-butylcalixarenes were used as sensitive layers. Materials in powder form were synthesized at the Institute of Organic Chemistry of NASU and kindly provided by prof. V.I. Kalchenko. The films were obtained by thermal evaporation in vacuum (with the VUP-5M setup, residual pressure of 5×10^{-4} Pa) and deposition onto the metal electrodes of piezoelectric transducers [22], or onto

the polished silicon substrate 20x20 mm in size for optical transducers [23], in both cases at room temperature (297±2 °K). The average deposition rate was about 10 nm·min^{-1}. The films thickness was monitored during deposition by means of quartz thickness measuring device; the final thickness obtained for all cases was about 200 nm.

The following groups of organic compounds were used as analytes: chlorinated compounds (chloroform, dichlorethane), aromatic compounds (toluene, xylene), ketones (acetone), ethers (butylacetate) and alcohols (ethyl, isopropyl and butyl alcohol).

Experimental setup and measurement principles

In this work for direct experimental evaluation of organic compounds vapor adsorption onto the calixarene coatings, the 5-channel multisensor system based on AT-cut quartz resonators (with resonance frequency of 10 MHz) was used [22]. Upon adsorption of the analyte molecules on sensitive layer the working frequency of quartz resonator decreases. Basic equation describing the relation between the change in resonance frequency of AT-cut quartz crystal and the mass adsorbed on the crystal surface is according to [24, 25]

$$\Delta f = -\frac{2 f_0^2}{A \sqrt{\rho_q \mu_q}} \Delta m \qquad (1)$$

where Δf is the change in crystal oscillation frequency in Hz, f_0 is the piezoquartz frequency in MHz, Δm is the mass adsorbed on the sensitive film, g, A is the electrode surface area in cm^2, ρ_q = 2.648 g·cm^{-3} (the quartz density), μ_q = 2.947×10^{11} g·cm^{-1}·s^{-2} (the AT-cut quartz shear modulus).

For additional investigation of vapor adsorption onto the calixarene layers we used the optoelectronic interference multisensors with digital response registration in form of change in the color components (red, green and blue) of the interference-colored calixarene layers upon the adsorption of analyte molecules [23]. The sensor system included the white light source, device for image capturing (web camera) and the flow-type cell with the sensor array [26]. It was shown earlier, that the calixarene films can be used as sensitive layers in colorimetric gas sensor for detection of alcohol molecules of several types [27], chlororganic and aromatic compounds [28]. Interference coloration of the thin layer of sensitive coating deposited on reflective substrate

changes upon interaction with gas molecules due to change in refraction index and thickness of the film. Usually a change of the color vector length in the R, G, B values space is used as response of such colorimetric sensor [26]. However, as numerous experiments have shown, the calculation of angular coordinates of the color vector in above mentioned space provides more accurate representation of the colorimetric image of the film; this is achieved due to compensation of instability caused by fluctuations of the light source intensity and by noise in the data transmission channel [29]. Thus, we will define the response of interference colorimetric sensor upon the influence of analyte vapor as deviation of angular position of the color vector from its previous state [28]:

$$\Delta S = \sqrt{\left[\frac{R_1}{L_1} - \frac{R_0}{L_0}\right]^2 + \left[\frac{G_1}{L_1} - \frac{G_0}{L_0}\right]^2 + \left[\frac{B_1}{L_1} - \frac{B_0}{L_0}\right]^2} \qquad (2)$$

where R, G, B are the measured values of the color vector components, $L = \sqrt{R^2 + G^2 + B^2}$ is the absolute length of the color vector in R, G, B space and indices 0 and 1 define the initial and subsequent states of the film (before and after its exposure to analyte vapor) respectively.

Methods of measurement

The colorimetric RGB-measurement method

The analyzed organic compound vapors with different concentrations were prepared by diluting the initial saturated vapors with dry air to the defined amount of dilution. Then the mixture was transported through the sampling cell with volume of 2 ml, where the sensor array with calixarene layers was installed. Table 1 shows concentration ranges for all used analytes as well as concentration change step value. Let us note that the maximum concentration listed in the table corresponds to 50 % dilution and the minimum concentration corresponds to 95 % dilution. The step at which the analyte concentration was increased corresponded to the 5 % change in analyte amount. The concentration value was calculated according to the following formula:

$$C = \frac{P_s}{P_{atm}} \frac{V_s}{V} 10^6 \qquad (3)$$

where C is the analyte concentration in ppm, P_s is the analyte saturated vapor pressure, P_{atm} is the nor-

mal atmospheric pressure (766 mm Hg), V_s is the volume of a saturated vapor sample, V is the volume at which the dilution was performed (a 20 ml syringe).

Table 1

Minimum and maximum concentration values for the investigated analytes vapor supplied to the sensor cell, and the step of concentration change during the concentration dependencies measurement.

Analyte	Saturated vapor pressure at 23 °C, mm Hg	Minimum concentration, ppm	Maximum concentration, ppm	Concentration change step, ppm
Acetone	202	13185	131850	13185
Butanol	5	290	2900	290
Butylacetate	18	1174	11740	1174
Chloroform	177	11553	115530	11553
Dichlorethane	75	4895	48950	4895
Ethanol	50.5	3296	32960	3296
Isopropanol	39	2545	25450	2545
Toluene	25.5	1664	16640	1664
Xylene	6	392	3920	392

Registration of the colored image of investigated sample was performed at room temperature, first for the initial state of the sample, then every second during ten seconds after the exposure to analyte vapors and then at the point 2 minutes after purging the sample with dry air. In all cases the coloration state after 10 seconds from the start of analyte vapor supply was taken as the response signal for further processing.

The quartz microbalance (QM) method

The necessary conditions for gas mixtures analysis is the consistency of their composition and concentration during the entire period of experiment. For each of the investigated samples, the concentration was calculated according to the values listed in Table 1; the sample then was injected into the 110 ml cell through the inlet. The analyte vapor filling the cell contacted the sensor array. With the help of multisensor system the quartz elements response kinetics was simultaneously recorded for all calixarene layers, sequentially for each analyte at the given concentration. Response was registered during 10 minutes, however in all cases the maximum response value was taken as informative parameter, that is, the maximum deviation of the resonator oscillation frequency from its initial value. The temperature during the measurement was maintained at 20 °C by means of thermostat [22]. To ensure the

equal measurement conditions and eliminate the influence of previous experiments after each measurement the cell was cleaned by blowing with carrier-gas (argon), which always lead to restoration of the sensors working characteristics.

Results and discussion

Using both the above described measurement methods, the responses for five types of calixarene films to the vapor of nine organic analytes in wide range of concentrations were obtained.

Fig.1 shows the calculated from formula (1) mass of adsorbed molecules for each of the investigated analytes depending on its concentration for QM-sensors based on respective calixarene layers.

Fig.2 shows the concentration dependencies for responses of optical RGB-sensors based on the same sensitive layers, calculated from formula (2). Let us note that the concentrations scale for each analyte for all presented curves is identical and corresponds to the data in Table 1.

As it could be seen from the presented curves, the responses of all investigated QM-sensors (which are proportional to the adsorbed molecules mass) show monotonous growth upon the increase of analyte concentration, and the mass increase rate varies depending on the analyte type. At the same time behavior of concentration dependencies for majority of RGB-sensors responses is somewhat different: with concentration increase the responses change insignificantly, and only after some threshold concentration the response value starts to increase quite rapidly. Such response behavior is typical for C[3]A, C[6]A and C[8]A films. Only the C[5]A calixarene demonstrates responses close to linear.

For more intuitive juxtaposition of QM and RGB-sensors sensitivity and selectivity Fig.3 shows normalized responses to investigated analytes at fixed concentration equal to $P_н/2$.

Reasoning from the present data, we may outline the following characteristic features of calixarene layers as sensitive materials that were equivalently evidenced in both types of sensors. First, all films appeared to be least sensitive to alcohol, especially in RGB-measurements. Second, the largest responses were observed for chlorinated analytes (chloroform, dichlorethane). Most sensitive in respect to all considered analytes are the C[5]A and C[6]A films, and the least sensitive is C[4]A.
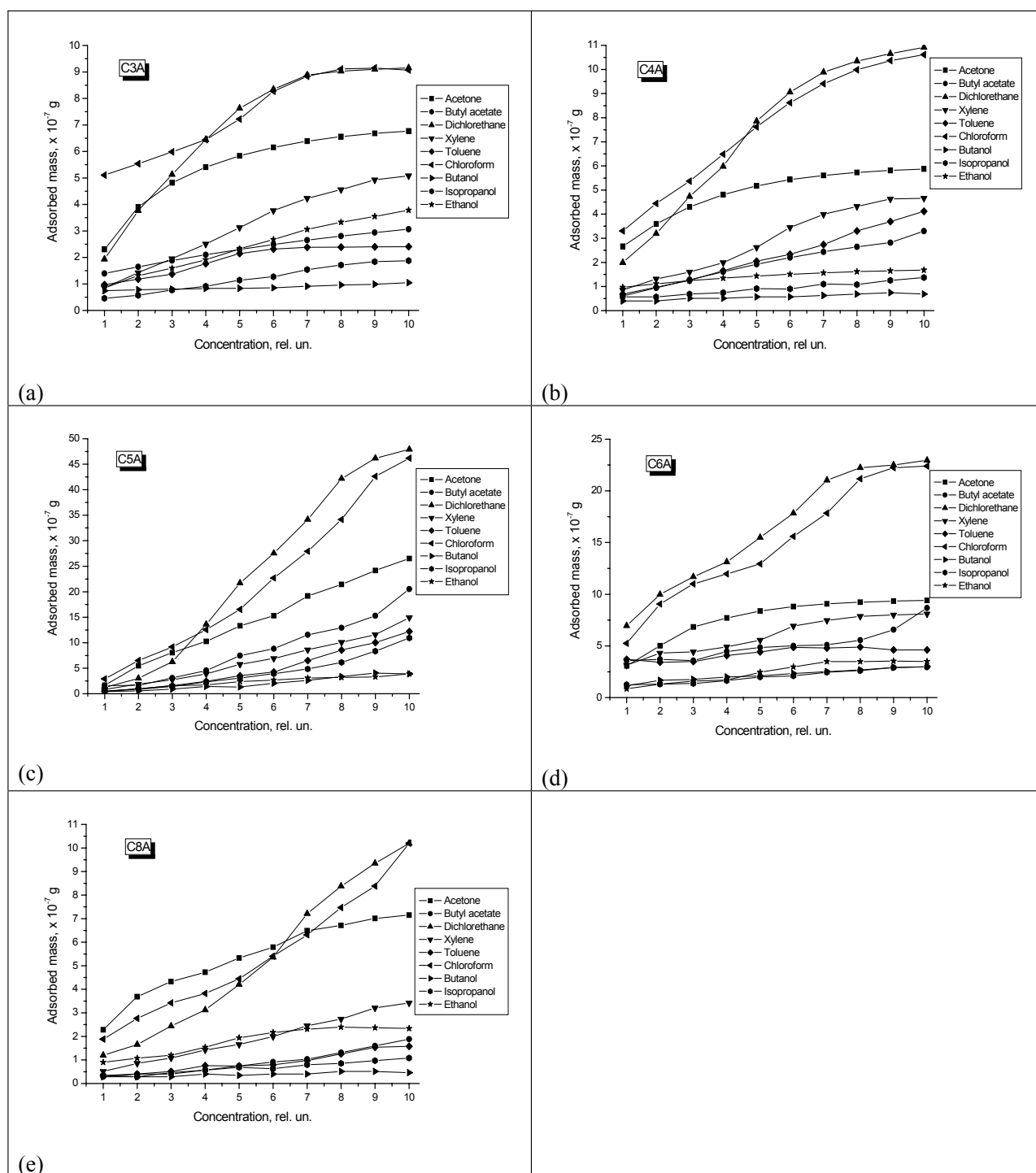
Fig. 1. Concentration dependencies for the mass adsorbed on calixarene layers of specified types for the entire set of investigated analytes: (a) C[3]A, (b) C[4]A, (c) C[5]A, (d) C[6]A, (e) C[8]A; concentration range for each of the given analytes are listed in Table 1.

To specific differences in responses of QM and RGB-sensors we may attribute the following: among the QM-sensors maximum absolute sensitivity to the majority of used analytes is observed for sensors with the C[5]A sensitive layer (see Fig.3,a). Less sensitive are the sensors with C[6]A layer (approximately by factor of two) and the least sensi-

tive are sensors with C[3]A, C[4]A, C[8]A layers (by factor of 4-5). At the same time RGB-sensors with different calixarene layers differ from each other not as much by sensitivity but more by dynamics of the sensitivity change depending on concentration. However, the sensors with C[5]A sensitive layer also stand out here demonstrating nearly linear dynam-

ic range of responses in considered concentrations range; on the contrary, sensors based on the C[4]A

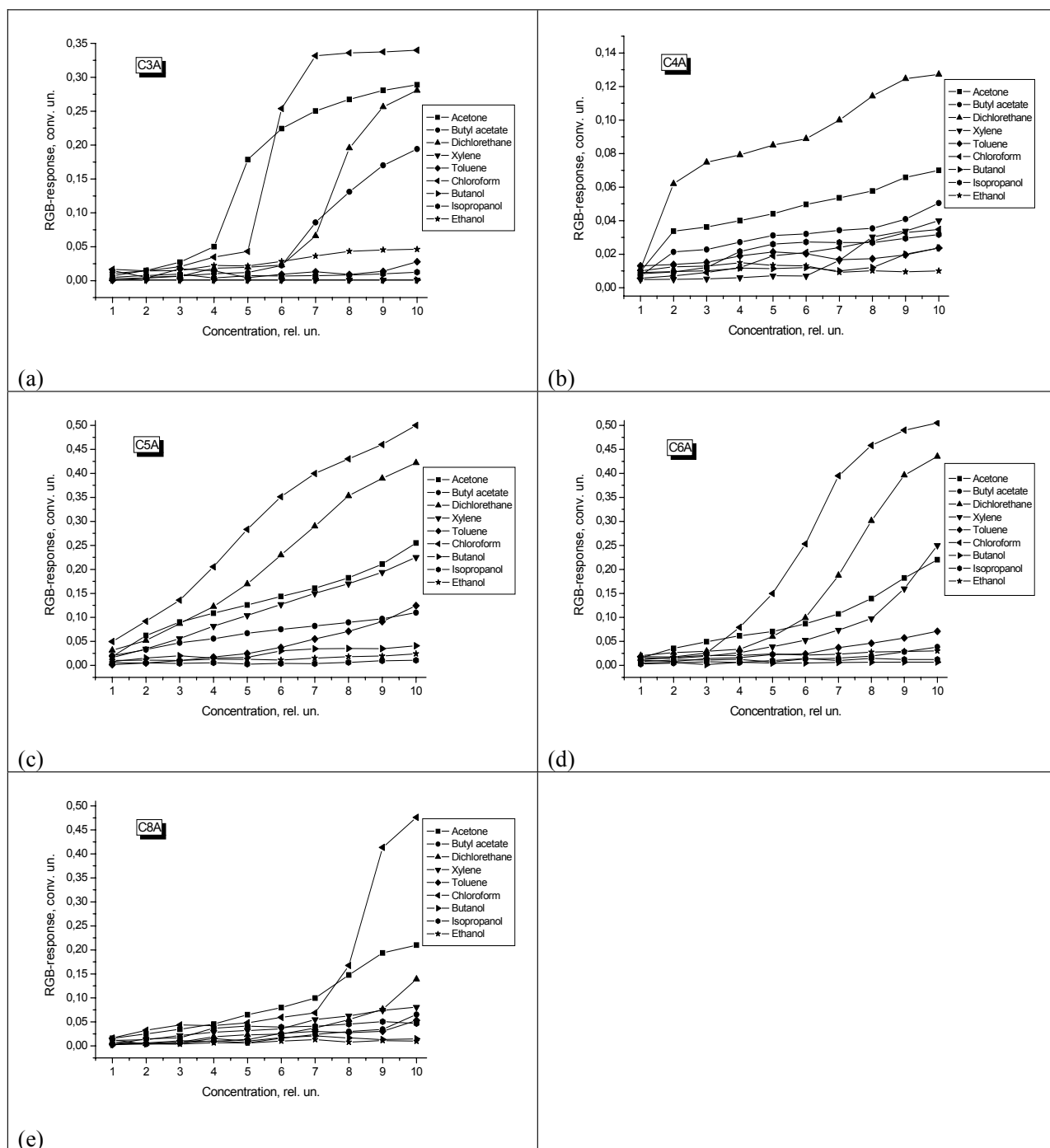film demonstrate weak reaction to all analytes at any concentrations.

Fig. 2. Concentration dependencies for responses of the RGB-sensors with sensitive layers formed with calixarenes of five types to the vapor of specified analytes: (a) C[3]A, (b) C[4]A, (c) C[5]A, (d) C[6]A, (e) C[8]A; concentration range of the analytes are listed in Table 1.

When analyzing the obtained responses, one has to keep in mind that variation of concentration in experiments was achieved by dilution of saturated vapor, and since the saturated vapor pressure for considered analytes significantly varies (see Table 1), the concentration scale is actually different for different analytes.

However, from the diagrams in Fig.3, one may notice that the magnitude of response to various analytes is not proportional to their concentration

and even not correlate with it. E.g. responses to the acetone vapor (P_s = 202 mm Hg) are equal to responses to butyl acetate (18 mm Hg) and xylene (6 mm Hg) and approximately 2 times lower than responses to dichlorethane (75 mm Hg) and chloroform (177 mm Hg).
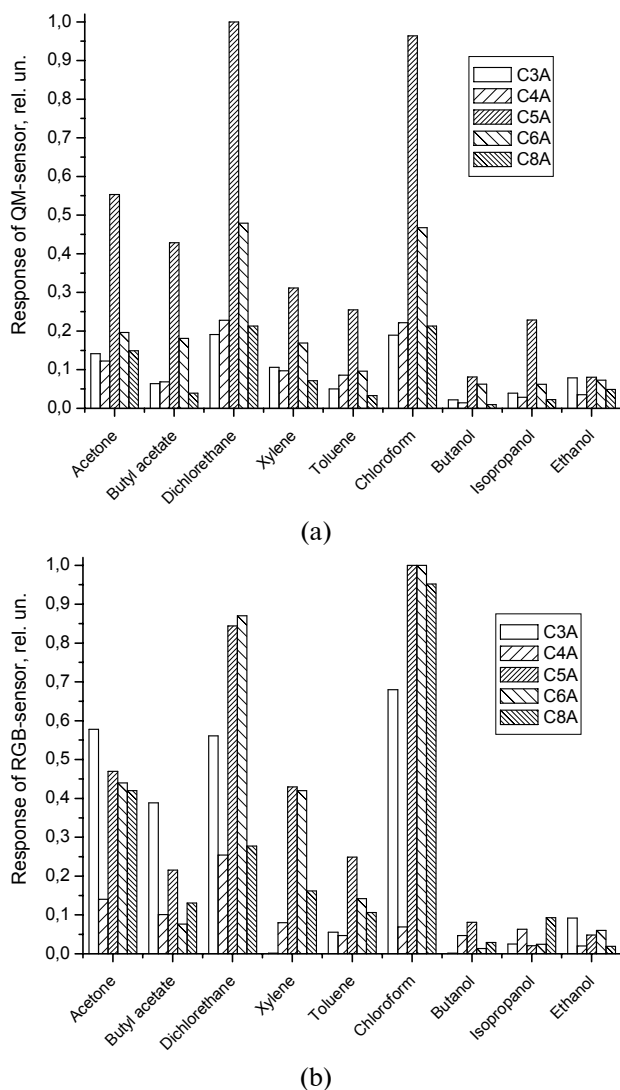

(a)

(b)

Fig. 3. Relative responses of QM-sensors (a) and RGB-sensors (b) with sensitive layers of C[3]A, C[4]A, C[5]A, C[6]A, C[8]A to the vapors of all investigated analytes at fixed concentration of P_s/2.

Obviously, the individual selective properties of the "analyte — sensitive layer" system play more important role than the analyte concentration.

Regenerative properties of calixarene sensitive layers upon the influence of organic compounds vapor were also investigated. Fig.4 shows (by the example of sensor with C[5]A layer) the RGB-sensor regeneration curves (that is, the return to initial baseline after exposure to the analyte vapor at various concentrations and subsequent purging with

dry air). The results indicate high reproducibility of responses in a wide range of concentrations (300 through 100000 ppm, depending on analyte). Similar data were also obtained for sensors with sensitive layers of other types.
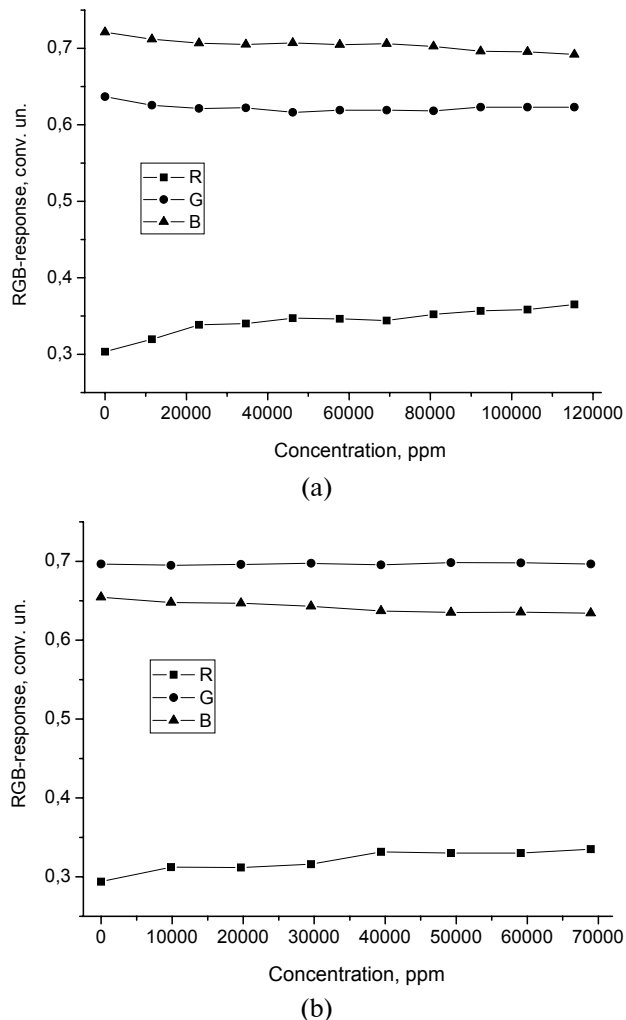

(a)

(b)

Fig. 4. Regeneration curves for RGB-sensor with the C[5]A sensitive layer, characterizing the return of the film color to its initial state after the exposure to acetone (a) and chloroform (b) vapor in various concentrations and subsequent purging with dry air.

It has to be mentioned that in both types of measurement that was conducted at room temperature after purging and regeneration of sensor element the informative parameter magnitude (the film color or quartz resonator frequency) practically always returned to its initial value, which indicates the absence of strong chemical bonding of molecules within the calixarene films, that is the interaction is characterized by rather weak (coordination, van der Waals) bounds.

As could be seen from the responses of QM and RGB-sensors (see Fig.3), the different calixarene

layers has overlapping but at the same time quantitatively different sensitivity to investigated analytes. This fact could be put to the base of development of the multielement multiparametric sensor for organic substances based on the sensitive films of various calixarenes, when the output signals from each separate sensor element are being registered and form the multidimensional response, which is then to be processed with the help of statistical pattern recognition techniques.

Each analyte or mixture forms its own unique chemical image, which can be mathematically represented, transformed and compared to other images. Fig.5 shows the result of processing the obtained 5-dimensional response vectors from the array of five QM-sensors and five RGB-sensors respectively, by means of principal component analysis [30]. This method allows do reduce the dimensionality of the initial data to two dimensions and visualize it with convenient graphical representation on the principal coordinates plane. Each point on the plane corresponds to one of the analytes at specific concentration and the series of one-kind points corresponding to different concentrations forms certain chemical image of the given analyte occupying a certain region. Absence of overlapping regions would indicate the high selectivity of the sensor array.

As could be seen, in our case reliable discrimination is possible for chlororganic compound and acetone for both sensor arrays, other analytes are more difficult to discriminate, especially at small concentrations. The better selectivity results are demonstrated by the QM-sensors array, probably due to wider range of sensitivity to various analytes.

Comparative analysis of QM and RGB-sensor responses

If one compare the diagrams of the sensor responses for QM and RGB-sensors to the entire set of used analytes (see Fig.3,a,b), one could notice a certain similarity at least in general tendency of change that's why we may suppose that there exists a correlation between the magnitudes of these responses. The reason for this assumption is that the both sensor types used the same calixarene films as sensitive layers, of the same thickness and obtained with identical technology. Besides, the measurement conditions for quartz and optical sensors were also chosen to be identical. The physical and

chemical processes taking place upon adsorption of the analyte vapor onto the sensitive layer are also identical.
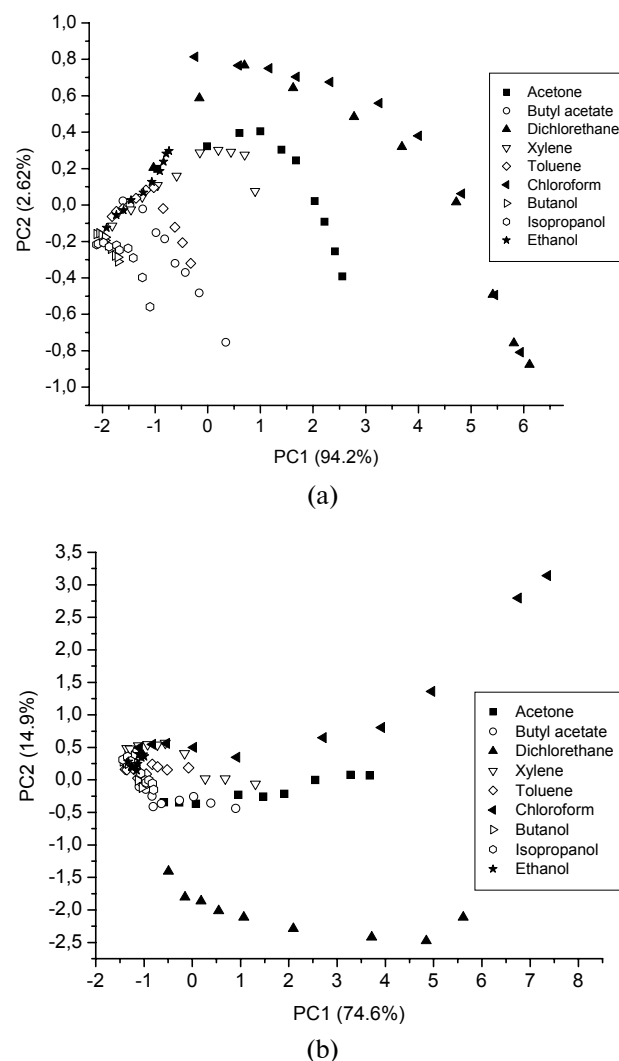

(a)

(b)

Fig. 5. Disposition of the investigated analytes images on the principal coordinates plane for the five QM sensors array (a) and five RGB-sensors array (b); as the source statistic for calculation all available response values shown in Fig.1 and 2 were used.

Thus, it would be interesting to compare the responses of two types of sensors to find out the grade of similarity in responses caused by identical processes, that is to find out if there exists correlation between the adsorbed molecular mass and corresponding change in optical parameters for each of the investigated sensitive films.

Using all the available response values for QM and RGB-sensors obtained in the experiments, the two-dimensional response diagrams were built for all investigated calixarene films used as sensitive layers for respective sensors (Fig.6). As can be seen, the registered distribution statistics shows general ten-

dency of simultaneous increase on both axes, that is the positive correlation between the QM and RGB-responses. Table 2 lists the calculated correlation coefficients for each type of calixarene film over the various data sets, namely (a) by the whole totality of collected responses, (b) separately by each fixed concentration for all analytes and (c) separately by each analyte for all its concentrations.
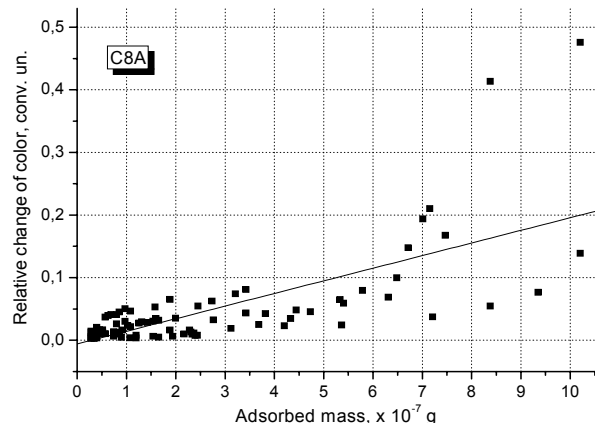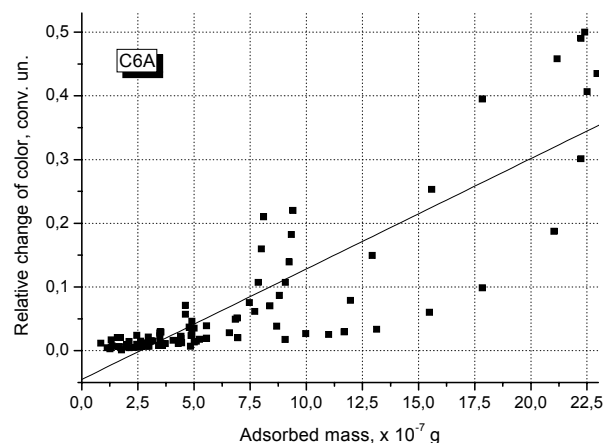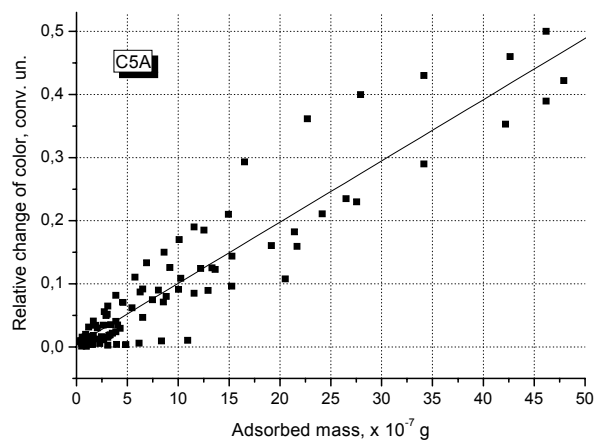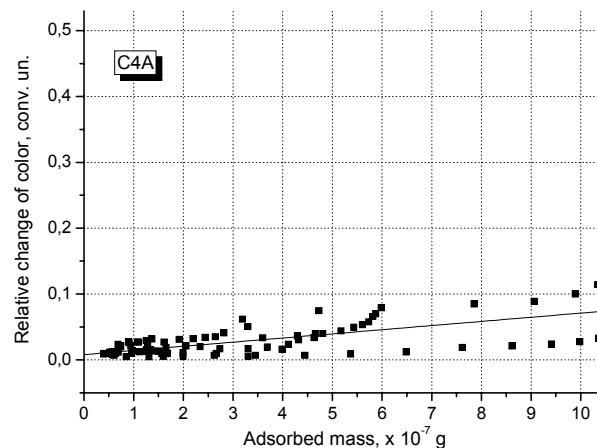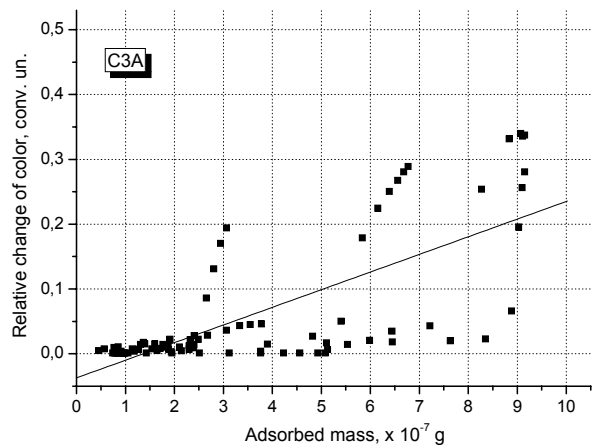

Fig. 6. Correlation diagrams for QM and RGB-sensor responses for five types of the investigated sensitive calixarene films; straight lines show the least squares linear approximation of the obtained data.

For further analysis let us denote the following. Used calixarenes, being the volumetrically porous organic materials, are composed of cyclic macromolecules having a cup-like shape and the nanocavities between them. The volatile analyte molecules easily penetrate to the bulk of the film.

Basing on the concept that this leads either to the film material the density increase due to the increasing number of particles per unit of volume, when the analyte molecules are being bound within the film, or the organic film swells as a result of adjacent film fragments being pushed aside by the embedding analyte molecules [26-28], we could assume that in the first case such interaction leads to increase of the refraction index of the film and in the second case to increase of the film thickness. This model is confirmed by the papers [31, 32], where it is shown that the contact of calixarene films with saturated vapor of benzene, toluene and chloroform may lead to the increase of film thickness by 10-20 % and/or increase of its refraction index by 0.01-0.1.

Table 2

Correlation coefficients for QM and RGB-sensor responses calculated for each type of calixarene film over the following data sets: whole totality of the obtained responses, by every fixed concentration for all analytes, and by every analyte for all its concentrations.

Calixarene	C[3]A	C[4]A	C[5]A	C[6]A	C[8]A	Calculation method
Correlation coefficient $r(S_{RGB}, S_{QM})$	0.726	0.637	0.935	0.862	0.709	Over entire data set
	0.773	0.374	0.910	0.823	0.681	Averaging by concentrations
	0.616	0.497	0.924	0.778	0.821	Averaging by analytes

Now we need to relate the magnitude of RGB-sensor response calculated from (2) to a change of optical parameters of the thin film — thickness d, refraction index n and their product nd. Simulation of the response for three-layer thin film system with Frenel equations with varying optical parameters of the film [33] in vicinity of the used calixarene films parameters $n = 1.5$ and $d = 200$ nm shows that with the increase of parameters by the above mentioned relatively small deviations of thickness and refraction index the colorimetric response magnitude increases monotonically with the change of nd product. This means that we can unambiguously relate the RGB-sensor response to the change in the film optical parameters.

Returning to the two-dimensional response diagrams for QM and RGB-sensors (see Fig.6), we may state the positive correlation between the changes in optical parameters and adsorbed mass in general for all considered calixarene films. However, from the Table 2, it follows that the correlation strength significantly differs for different films: it is profoundly maximal for C[5]A layers independently of calculation method, a little lower for C[6]A, intermediate correlation is observed for C[3]A and C[8]A layers, and the minimum correlation in all cases is characteristic for C[4]A layers.

We may suppose that the presence of strong correlation between QM and RGB-responses, that is the synchronous change in adsorbed mass and the nd parameter of the film, indicates that the whole bulk of the film is involved into adsorption process, being uniformly filled with the analyte molecules. This effect is most pronounced for the C[5]A films.

If the correlation is weak, it is logical to assume that molecules mostly accumulate on the surface of the film and do not penetrate into the bulk. This effect, as we can see, is mostly characteristic for the C[4]A films. Considering the C[3]A, C[6]A and C[8]A films, we may assume that both adsorption types may take place.

Conclusion

Obtained results allow to predict which of the investigated sensitive materials may be promising for use in the sensory systems for specific applications. It is shown that the most sensitive type of calixarene layers for all considered analytes appear to be the C[5]A and C[6]A films, and the least sensitive is C[4]A. At this, for classification of the chlorinated chemical compounds most sensitive and promising are the layers based on the C[5]A calixarene.

It is shown that with the increase of concentration of the analytes the mass of adsorbed molecules for all investigated calixarene films gradually aggregates on the films however for different films at a different rate. At the same time optical parameters of the C[3]A, C[4]A, C[6]A and C[8]A films change insignificantly and only start to rapidly increase after the exceeding of a certain concentration threshold, which varies depending on both calixarene and analyte types.

For the C[5]A layers optical parameters change quite synchronously with the growth of adsorbed mass. The positive correlation between the change of these parameters is strongest for the C[5]A layers (0.93) and weakest for the C[4]A layers (0.63).

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