

## Sorption of azo dyes from aqueous solutions by tetradodecyloxybenzylcalix[4]resorcinarene derivatives

Ella Kh. Kazakova · Julia E. Morozova ·  
Diana A. Mironova · Alexander I. Kononov

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**Abstract** Four water-insoluble tetradodecyloxybenzyl calix[4]resorcinarenes with various functional groups at the upper macrocycle rim (unsubstituted calix[4]resorcinarene **1**, carboxylic acid derivative **2**, ethyl ester derivative **3** and aminoethylamide derivative **4**) were synthesized and tested as sorbents for water-soluble azo dyes methyl orange (MO), acid orange 5 (AO 5) and congo red (CR) by solid–liquid extraction method without background electrolyte. It was observed that the sorption of azo dyes reaches 99% for sorbent **4**, which is partial protonated in contact with water and becomes able to electrostatic interactions with the dyes. It was demonstrated that calixresorcinarene **4** has the excellent sorption capacity for AO5 (130.5 mg dye per g of sorbent) due to effective calixresorcinarene–dye association in equal molar ratio mode.

**Keywords** Calix[4]resorcinarene · Azo dye · Sorption · Sorption capacity

### Introduction

The treatment of industrial wastewater was and is one of the major ecological problems. For coloring of plastics, textile, cosmetics, and paper, the industry still uses water-soluble dyes that are toxic for living organisms [1]. The majority of anionic dyes, including azo dyes examined in the present work, could not be biochemical oxidized, and therefore are removed from wastewaters by means of physical or chemical treatment. One of the most efficient

and inexpensive methods for removal of the dyes out of wastewaters is a solid–liquid extraction with inorganic or organic sorbents of natural or synthetic origin, such as, silica beads, activated charcoal, zeolites, and polyamies.

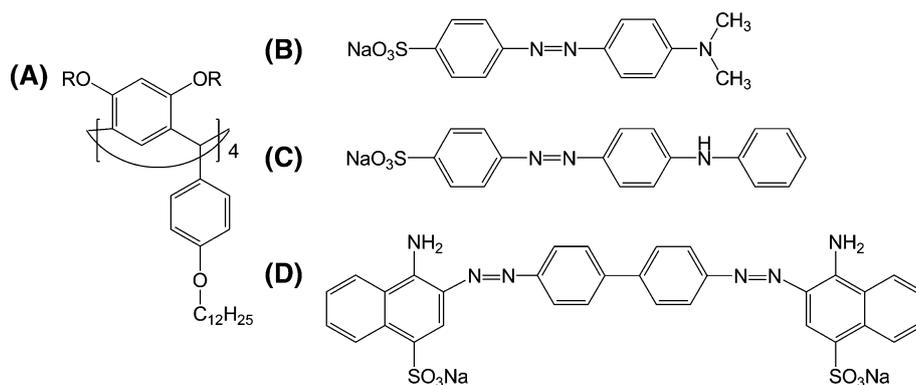
Quite recently, one of supramolecular macrocycles varieties—calixarenes—became to be used as a synthetic sorbents [2–7]. These compounds possess the aromatic cavity capable of CH– $\pi$ ,  $\pi$ – $\pi$ , and cation– $\pi$  interactions with guest molecules providing their efficient binding. At the same time, rather rigid framework of calixarenes presents a suitable platform for introduction of functional groups, that depending on their structure, could participate in hydrogen-bonding or electrostatic interactions [8, 9]. All this makes calixarenes and the related calixresorcinarenes a popular class of synthetic receptors.

Several authors describe the use of calix[*n*]arene derivatives as synthetic sorbents for azo dyes [10–18]. Oligomeric macrocycle derivative, prepared by condensation of *p*-*tert*-butylcalix[4]arene with hexamethylene diisocyanate, demonstrated a sorption capacity of 17 and 18% towards two azo dyes, *Titanium Yellow* and *Direct Blue 15*, respectively [10, 11]. *p*-*tert*-Butylcalix[6]arenes and *p*-*tert*-butylcalix[8]arenes with unsubstituted hydroxy-groups at the upper rim and ester or carboxylic groups at the lower rim were used for extraction of *Evans Blue*, *Direct Blue 15*, and *Direct Blue 1* [12]. The absorbance of the latter was most efficient in case of carboxylic substituents at the lower rim and reached 96 and 89% for calix[6]- and calix[8]arenes, respectively.

Here we report on the results of the study of calix[4]resorcinarenes **1–4** (Fig. 1) as sorbents for solid–liquid extraction of three water-soluble azo dyes methyl orange (MO), acid orange 5 (AO 5), and congo red (CR) from their aqueous solutions.

E. Kh. Kazakova (✉) · J. E. Morozova ·  
D. A. Mironova · A. I. Kononov  
A.E. Arbuzov Institute of Organic & Physical Chemistry,  
RAN KSC, Kazan, Russia 420008  
e-mail: ella@iopc.ru; frufu3@mail.ru

**Fig. 1** Chemical structures of the calix[4]resorcinarene (A),  $R = -H$  (1);  $R = -CH_2C(O)OH$  (2);  $R = -CH_2C(O)OCH_2CH_3$  (3);  $R = -CH_2C(O)NHCH_2CH_2NH_2$  (4) and the examined dyes: methyl orange MO (B), acid orange 5 AO 5 (C), congo red (D)



## Materials and methods

Tetradodecyloxybenzylcalix[4]resorcinarene **1** and its derivatives **2–4** were synthesized according to the procedure described earlier [19, 20]. Methyl orange (MO), acid orange 5 (AO 5), and congo red (CR) were from Sigma-Aldrich (Moscow, Russia). The purity of the dyes was verified with their absorbance spectra and they were used without any additional purification. All experiments were done in deionized water (3.5  $\mu\text{Om/cm}$ ).

IR-spectra were recorded with Bruker Vector 22 FT-IR Spectrometer (Bruker Optics, USA). UV-Vis spectra were recorded on Lambda 35 UV-VIS Spectrometer (Perkin-Elmer Instruments, USA) using quartz cells with the optical path of 1.0, 0.5 and 0.1 cm. All spectra were referenced against solvent blanks containing all components except for the dyes. The pH of aqueous solutions was measured at 20 °C with Thermo pH-meter (Thermo Electron, USA).

## Dye sorption

0.01 g of the macrocycle was placed either in 4 mL of dye aqueous solution or of deionized water (absorbance reference); the dye concentration was in the range of 0.01–0.02 mM. The solution was then mixed for 1 h at a rate of 360 rpm. After 24 h, the solution was centrifuged for 10 min at 5 krpm to separate the sorbent. The supernatant spectra were recorded against the aqueous solution obtained treated with the macrocycle. Dye concentration in the aqueous solution before ( $C_{\text{Dye}}^0$ ) and after ( $C_{\text{Dye}}$ ) its contact with the macrocycle was determined with the calibration graphs using the maximum intensity of the absorbance band: 464 nm for MO, 441 nm for AO 5, and 497 nm for CR. The sorption,  $\beta$ , was calculated as:

$$\beta = \frac{C_{\text{Dye}}^0 - C_{\text{Dye}}}{C_{\text{Dye}}^0} \cdot 100\%$$

For macrocycle **4**, that demonstrated a high efficiency of azo dye sorption, the concentrations of the feeding

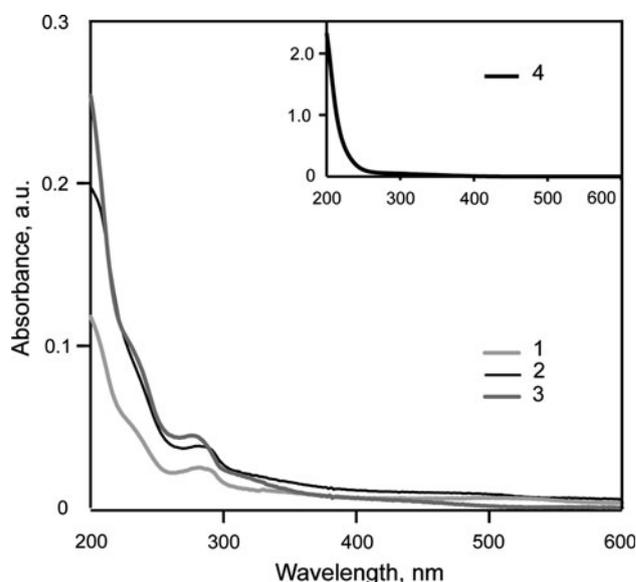
solutions were increased up to 0.08 mM for MO and CR and up to 0.89 mM for AO 5. The molar ratio  $v_{\text{CA}}/v_{\text{Dye}}$  of the macrocycle and dye was calculated along with specific sorption capacity,  $\alpha$  (mg/g):

$$\alpha = \frac{C_{\text{Dye}}^0 - C_{\text{Dye}}}{m} \cdot V,$$

where  $V$  is a volume of the dye solution in ml and  $m$  is a mass of the loaded macrocycle **4** (g).

## Effect of contact time on dyes sorption on sorbent **4**

2.5 mL of 0.002 or 0.02 mM dyes solution was placed in 1 cm optical cell and 0.001 g of **4** was added so that it stayed at the surface of solution. The spectra were recorded for unstirred solutions at 20 °C and sorption,  $\beta$ , was calculated for each of them.



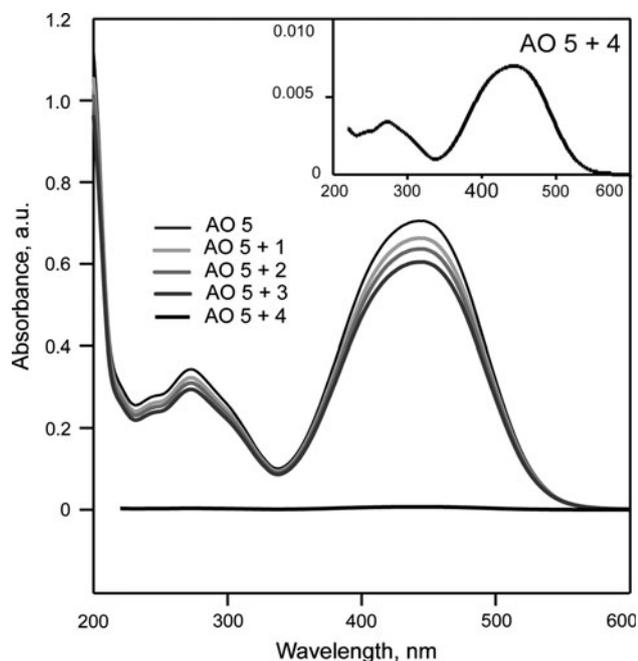
**Fig. 2** UV-vis spectra of aqueous solutions of **1–3** after the macrocycle solubility experiments ( $l = 1.0$  cm, 20 °C). Inset the same data for **4** ( $l = 0.1$  cm, 20 °C)

**Table 1** Sorption of azo dyes by examined macrocycles ( $m_{1-4} = 0.01$  g;  $V_{\text{dye}} = 4$  mL)

Macrocycl	MO		CR		AO 5	
	$C_{\text{Dye}}^0$ (mM)	$\beta$ (%)	$C_{\text{Dye}}^0$ (mM)	$\beta$ (%)	$C_{\text{Dye}}^0$ (mM)	$\beta$ (%)
1	0.019	<1	0.012	<1	0.009	6
2	0.011	4	0.013	3	0.008	4
3	0.009	<1	0.017	8	0.009	5
4	0.009	98	0.017	>99	0.016	>99

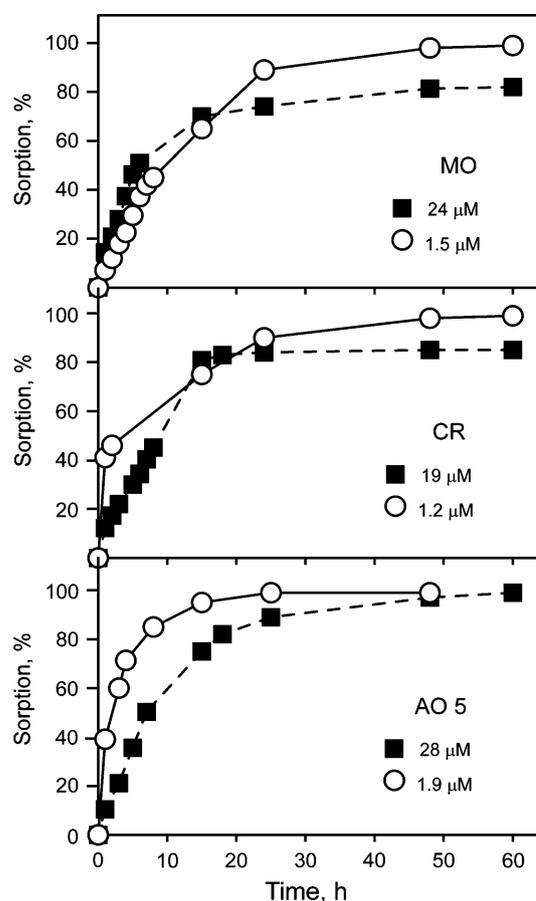
## Results and discussion

The macrocycles **1–4** taken for the present study have a very limited solubility in water. Their UV–vis spectra in deionized water given on Fig. 2 demonstrate that the presence of the macrocycle in aqueous solutions could be verified by the presence of their characteristics bands in the range of 200–400 nm. Among four macrocycles, **4**, that is insoluble in such conventional organic solvents as methanol, chloroform, or DMSO, demonstrates the best solubility. Moreover, at  $\text{pH} < 5$  it is completely soluble in water. Even insufficient solubility of this macrocycle in neutral aqueous solutions results in a shift of solution pH to basic range. For example, in a typical experiment addition of **4** to deionized water resulted in solution pH in the range of 8.8–9.5. **4** is the only one of four macrocycles capable of ionization in water, presumably due to a relatively low  $\text{p}K_a$  of its eight amidoamino-groups (the  $\text{p}K_a$  value of amino-groups of aminoethylamidated tetramethylcalix[4]resorcinarene [19] is  $9.66 \pm 0.10$  was theoretically determined

**Fig. 3** UV–vis spectra of AO 5 (0.02 mM) before and after sorption experiment

using Advanced Chemistry development (ACD/labs) software V8.19 (1994–2010 ACD/Labs)). Protonation results not only in a decrease of the hydrophobicity of the macrocycle, it enables **4** to participate in electrostatic interactions with dyes.

The sorption of the examined azo dyes by macrocycles **1–4** is summarized in Table 1. Note that even in 0.01–0.02 mM solutions the sorption of the dyes by neutral **1–3** does not exceed 8%, whereas for **4** it nears and even exceeds 90%. (see, for example, Fig. 3).

**Fig. 4** Effect of contact time on dyes adsorption on sorbent **4** ( $m_4 = 0.01$  g;  $V_{\text{dye}} = 2.5$  mL,  $20^\circ\text{C}$ )

**Table 2** Sorption of azo dyes by macrocycle **4** ( $m_4 = 0.01$  g;  $V_{\text{dye}} = 4$  mL;  $\text{pH}^0$  and  $\text{pH}$ —the pH-values of aqueous solution of azo dyes before and after sorption experiment)

Dye	$C_{\text{Dye}}^0$ (mM)	$C_{\text{Dye}}$ (mM)	$\beta$ (%)	$\alpha$ (mg/g)	$\alpha_{\text{mediia}}$ (mg/g)	$v_{\text{CA}}/v_{\text{Dye}}$	$\text{pH}^0/\text{pH}$
MO	0.082	0.008	90	9.7			7.8/8.8
	0.081	0.006	92	9.8	9.7	14	7.8/9.2
	0.081	0.007	91	9.6			7.8/9.4
CR	0.073	0.006	91	18.6			7.7/9.5
	0.078	0.002	97	21.2			7.7/9.4
	0.075	0.001	98	20.5	20.3	15	7.7/9.4
	0.075	0.002	97	20.3			7.6/8.8
	0.075	0.001	99	20.6			7.7/9.3
AO 5	0.069	0.069	>99	–	–	–	7.7/9.1
	0.129	0.129	>99	–	–	–	7.7/8.9
	0.890	0.035	96	128.3			7.7/9.5
	0.890	0.016	98	131.2	130.5	1	7.6/9.3
	0.890	0.011	99	132.0			7.7/9.2

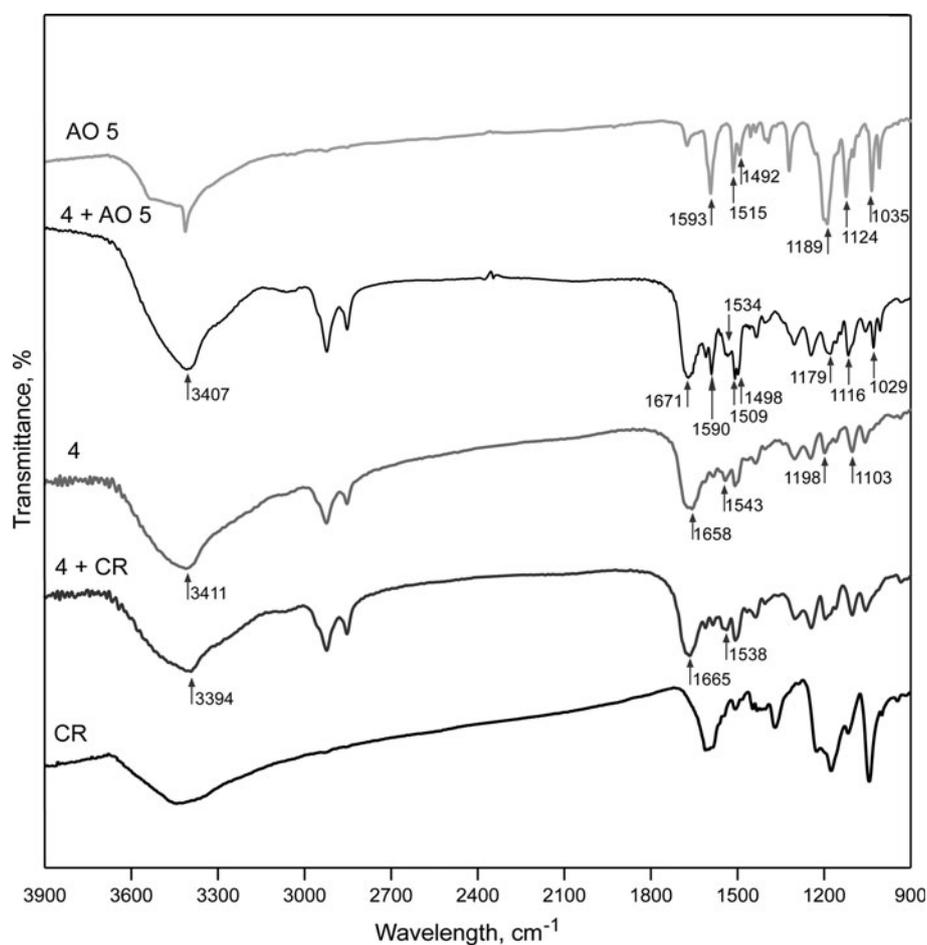
**Fig. 5** FT-IR spectra of AO 5; 1:1 associate of AO 5 and **4**; 1:15 associate of CR and **4**; and CR (in KBr pellets)

Figure 4 shows effect of contact time on sorption capacity of **4**, recorded in the absence of stirring. Apparently, diffusion plays a crucial role in the sorption of the dye: in first 2 h, it reached only 10–50%, whereas the maximum capacity was obtained after 24 h.

A high degree of sorption of **4** towards the dyes from their 0.01–0.02 mM solutions enabled to increase the concentration of the feeding solutions up to 0.08 mM for MO and CR and up to 0.89 mM for AO 5 without the loss of the sorption efficiency.

Increase of dye concentration in the feeding solution did not affect the efficiency of their sorption by **4**: in 0.08 and 0.89 mM of MO and AO 5 the sorption was 91 and 98%, respectively (Table 2). Characteristic sorption capacity calculated from the experiments was 9.5, 20.3, and 130.5 mg/g of the sorbent for MO, CR, and AO 5, respectively. It was calculated that dye: macrocycle molar ratio ( $v_{CA}/v_{Dye}$ ) in case of MO and CR is 14 and 15, whereas for AO 5 it is 1.

FT-IR spectra of the dyes and their associates with **4** isolated, dried, and doped in KBr pellets are summarized in Fig. 5. In associates of **4** with CR the macrocycle is present in a large excess and its spectra is, therefore, very similar to that of the macrocycle. Nevertheless,  $\nu_{NH}$  band of the associate is  $\sim 17\text{ cm}^{-1}$  shifted in a lower frequency range ( $3,394\text{ cm}^{-1}$ ), presumably, indicating the presence of an intermolecular hydrogen bond (IMHB) of amino-group. Amide I ( $1,665\text{ cm}^{-1}$ ) and II ( $1,538\text{ cm}^{-1}$ ) bands are also shifted to the lower frequency range, most probably, indicating the other participant of the IMHB.

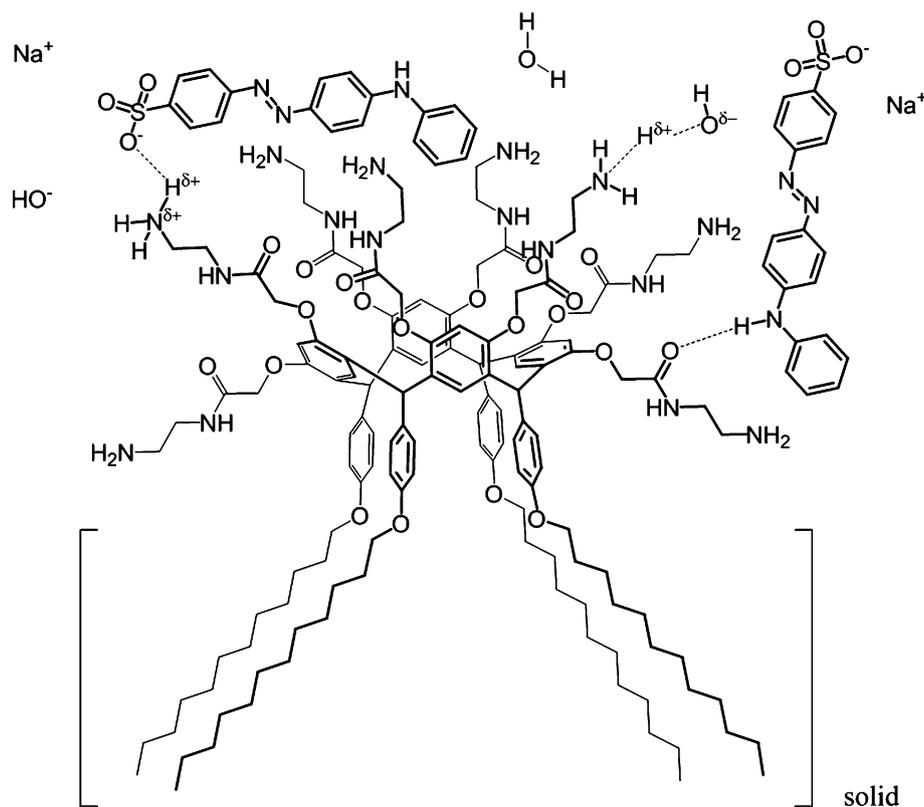
In the spectra of 1:1 associate of AO 5 and **4** both the dye and the macrocycle bands are present and some of them overlap. For those bands that do not overlap  $\nu(NH)$  ( $3,407\text{ cm}^{-1}$ ) and Amide I ( $1,671\text{ cm}^{-1}$ ) and II ( $1,534\text{ cm}^{-1}$ ) bands of calixarene and  $\delta(NH)$  ( $1,590\text{ cm}^{-1}$ ) and  $\nu(S=O)$  ( $1,179, 1,116, 1,029\text{ cm}^{-1}$ ) of the dye are shifted at lower frequencies. This suggests that

formation of the associate is accompanied by interactions of amine- and amide-groups of the macrocycle with aromatic amino-group and sulfo-group of the dye. The latter is negatively charged and amino-group of **4** is positively charged, indicating the sites for Coulomb interactions between the dye and the sorbent. That is, apparently responsible for greater dye sorbent capacity of **4**, as compared to **1–3**. The amido and amino groups of calixarene **4**, participating of the IMHB with molecule of dye also contribute to its sorption capacity. A similar improvement of azo dye sorption was observed in a polymeric sorbent upon introduction of amido-groups [21].

Besides the formation of inclusion complexes between the molecules of the sorbent and the azo-dyes can not be excluded (Fig. 6). A sorption capacity of **4** towards AO 5 about 13 and 6.5 times higher than for MO and CR, respectively. This may be explained by the most favorable steric conditions for the formation of inclusion complex. However, a low degree of azo-dyes sorption by compounds **1–3** indicates that while inclusion complex formation could affect the selectivity of the sorption and the sorbent capacity, its efficiency is provided by a lot stronger electrostatic interactions.

Sorbent **4** could be regenerated by washing in  $80\text{ }^{\circ}\text{C}$  DMSO. As a result, the solvent gets the color of the desorbed dye, whereas insoluble calixarene forms a white precipitate that could be easily separated, rinsed, and dried.

**Fig. 6** Proposed interactions of **4** and AO 5



## Conclusions

Thus, four calixresorciarene macrocycles of the same cavity size and with the same lower rim substituents were examined as sorbents for solid–liquid extraction of three azo dyes. It was found that the macrocycle with the upper rim groups capable of ionization, accompanied by its protonation, is the most efficient sorbent for the examined anionic dyes. Additionally, it was demonstrated that while strong Coulomb interactions provide the efficiency of the dye sorption, sorbent capacity and selectivity depend on specific macrocycle-dye interactions at molecular level.

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