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The chromatographic study of complexation of functionalized calix[4,8]arenes with aromatic aldehydes

Aim. To study the Host-Guest complexation of octakis(diphenoxyphosphoryloxy)-tetramethylcalix[4]resorcinarene (**PRA)**, 5,17-bis(N-tolyl-iminomethyl)-25,27-dipropoxycalix[4]arene (**IC4A**), 5,11,17,23-tetrakis(diisopropoxyphosphonyl)-25,26,27,28-tetra-propoxycalix[4]arene (**PC4A**) and oktakis(diethoxyphosphoryloxy)-tert-butylcalix[8]arene (**PC8A**) with benzaldehyde, salicylaldehyde, *p*-anisaldehyde**,** and veratraldehyde by RP HPLC and molecular modeling methods.

Results and discussion. The stability constants of Host-Guest complexes (K_A = 57 M^{-1} – 1649 M^{-1}) strongly depend on the calixarene structure and the aromatic aldehyde nature. The enhancement of the complexing properties of calixarenes is observed in the row of **PRA** < **IC4A** < **PC4A** < **PC8A.** The volume of the calixarene molecular cavity plays the most important role in binding of aldehydes.

Experimental part. The stability constants of calixarene complexes with aldehydes were determined by RP HPLC method in acetonitrile-water (80 : 20, v/v) solution. The RP HPLC analysis was performed using a LiChrosorb RP-18 column. Molecular modeling of calixarene complexes was carried out using a Hyper Chem 8.0 program.

Conclusions. The Host-Guest complexation data can be used as a useful tool in design of calixarene based sensor devices for determination of the aromatic aldehydes in air or preparation of chromatographic phases for analysis of aldehydes in solutions.

Key words: calixarenes; aromatic aldehydes; inclusion complexes; stability constants; liquid chromatography; molecular modeling

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Хроматографічне дослідження комплексоутворення функціоналізованих калікс[4,8]аренів з ароматичними альдегідами

Мета. У роботі методами ОФ ВЕРХ і молекулярного моделювання вивчено комплексоутворення типу Господар-Гість октакіс(дифеноксифосфорилокси)-тетраметилкалікс[4]резорцинарену (**PRA**), 5,17-біс(N-толіл-імінометил)-25,27-дипропоксикалікс[4]арену (**IC4A**), 5,11,17,23-тетракіс(діізопропоксифосфоніл)-25,26,27,28-тетрапропоксикалікс[4]арену (**PC4A**) і октакіс(діетоксифосфорилокси)-трет-бутилкалікс[8]арену (**PC8A**) з бензальдегідом, саліциловим альдегідом, *п*-анісовим альдегідом і вератровим альдегідом**.**

Результати та їх обговорення. Константи стійкості комплексів Господар-Гість (K_A = 57 M^{-1} – 1649 M^{-1}) значною мірою залежать від структури каліксарену і природи ароматичного альдегіду. Збільшення комплексоутворювальних властивостей каліксаренів спостерігається в ряду **PRA** < **IC4A** < **PC4A** < **PC8A.** Найбільш важливу роль у зв'язуванні альдегідів відіграє об'єм молекулярної порожнини функціоналізованого каліксарену.

Експериментальна частина. Константи стійкості каліксаренових комплексів з альдегідами визначали методом ОФ ВЕРХ у розчині ацетонітрил-вода (80 : 20, за об'ємом). ОФ ВЕРХ аналіз проводили з використанням колонки LiChrosorb RP-18. Молекулярне моделювання комплексів каліксарену здійснювали за програмою Hyper Chem, версія 8.0.

Висновки. Отримані результати з комплексоутворення функціоналізованих каліксаренів можуть бути використані як інструмент у розробці сенсорних пристроїв на основі каліксарену для визначення альдегідів у повітрі, а також у виготовленні хроматографічних фаз для аналізу альдегідів у розчинах.

Ключові слова: каліксарени; ароматичні альдегіди; комплекси включення; константи стійкості; рідинна хроматографія; молекулярне моделювання

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Хроматографическое исследование комплексообразования функционализованных каликс[4,8]аренов с ароматическими альдегидами

Цель. В работе методами ОФ ВЭЖХ и молекулярного моделирования изучено комплексообразование типа Хозяин-Гость октакис(дифеноксифосфорилокси)-тетраметилкаликс[4]резорцинарена (**PRA**), 5,17-бис(N-толил-иминометил)-25,27-дипропоксикаликс[4]арена (**IC4A**), 5,11,17,23-тетракис(диизопропоксифосфонил)-25,26,27,28-тетрапропоксикаликс[4]арена (**PC4A**) и октакис(диэтоксифосфорилокси)-трет-бутилкаликс[8]арена (**PC8A**) с бензальдегидом, салициловым альдегидом, *п*-анисовым альдегидом и вератровым альдегидом**.**

Результаты и их обсуждение. Константы устойчивости комплексов Хозяин-Гость (K_A = 57 M^{-1} – 1649 M^{-1}) в значительной степени зависят от структуры каликсарена и природы ароматического альдегида. Повышение комплексообразующих свойств каликсаренов наблюдается в ряду **PRA** < **IC4A** < **PC4A** < **PC8A.** Наиболее важную роль в связывании ароматических альдегидов играет объем молекулярной полости функционализованного каликсарена.

Экспериментальная часть. Константы устойчивости каликсареновых комплексов с альдегидами определяли методом ОФ ВЭЖХ в растворе ацетонитрил-вода (80 : 20, по объему). ОФ ВЭЖХ анализ проводили с использованием колонки LiChrosorb RP-18. Молекулярное моделирование комплексов каликсарена осуществляли с помощью программы Hyper Chem, версия 8.0.

Выводы. Полученные результаты по комплексообразованию функционализованных каликсаренов могут быть использованы при розработке сенсорных устройств для определения ароматических альдегидов в воздухе, а также при изготовлении хроматографических фаз для анализа альдегидов в растворах.

Ключевые слова: каликсарены; ароматические альдегиды; комплексы включения; константы устойчивости; жидкостная хроматография; молекулярное моделирование

Calix[n]arenes [1] are three-dimensional macrocyclic compounds constituted by phenolic fragments linked *via* methylene bridges. In the 90s David Gutsche developed the preparative one-pot synthesis of the *tert*-butylcalix[4,6,8]arenes based on precision cyclocondensation of *tert*-butylphenol with formaldehyde (or paraform) in the presence of catalytic amounts of sodium hydroxide or potassium hydroxide. In the calixarene molecule conditionally the upper (wide) rim and the lower (narrow) rim are distinguished. The calixarene family extends to calix[4]resorcinarenes easily synthesized by cyclocondensation of resorcinol with aliphatic or aromatic aldehydes catalyzed by hydrochloric acid.

Calixarenes are easily amenable for chemical modification at the upper or the lower rim of the macrocycle. Due to the nanosized three-dimensional architecture, calixarenes functionalized with appropriate groups can be recognized with high selectivity, bind in supramolecular complexes and separate cations, anions, gases, neutral organic molecules, and biomolecules with the similar properties [2]. The supramolecular complexes can be stabilized by various non-covalent interactions, such as hydrogen bonds, π-π, CH-π, cation-π, anion-π, van der Waals, solvatophobic interactions, etc. The unique receptor properties provide broad prospects for the practical use of calixarenes in different fields of chemistry, biology, physics, nanotechnology [3-17].

In this paper the Host-Guest complexation of octakis(diphenoxyphosphoryloxy)-tetramethylcalix[4]resorcinarene (**PRA)**, 5,17-bis(N-tolyl-iminomethyl)-25,27-dipropoxy-calix[4]arene (**IC4A**), 5,11,17,23-tetrakis(diisopropoxyphosphonyl)-25,26,27,28-tetrapropoxycalix[4]arene (**PC4A**) and oktakis(diethoxyphosphoryloxy)-tert-butylcalix[8]arene (**PC8A**) with benzaldehyde **1**, salicylaldehyde **2**, *p*-anisaldehyde **3,** and veratraldehyde **4** (Scheme) was studied by RP HPLC and molecular modeling methods.

Since the aromatic aldehydes are widely used as starting materials or aromatic ingredients in pharmaceutical and cosmetics industry [18, 19], the Host-Guest complexation data can be used as a useful tool in design of calixarene based sensor devices for determination of the aromatic aldehydes in air or preparation of chromatographic phases for analysis of compounds in solutions.

Results and discussion

Complexation of the calixarenes with aldehydes was studied in the acetonitrile-water solution by the RP HPLC method using the approach previously developed [20, 21]. The stability constants of calixarene complexes were calculated from the dependence of the aldehyde retention factor on the concentration of calixarenes in the mobile phase.

The calixarene additives to the mobile phase decrease the retention factors k' of aldehydes **1-4** due to formation of the Host-Guest inclusion complexes. The linear plots of $1/k'$*vs* the calixarene concentration (Fig. 1-4) indicates formation of the Host-Guest supramolecular complexes with stoichiometry of 1 : 1 and allows using the equation (1) for calculation of their stability constants K_A:

$$1/k' = 1/k_0' + \mathrm{K_A} \times [\mathrm{CA}]/k_0', \qquad (1)$$

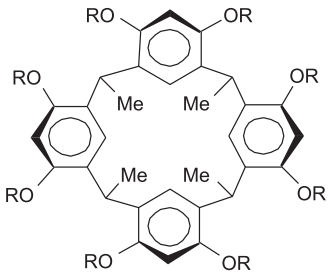
where k_0' і k' – are capacity factors of the aldehyde molecule determined in the absence and the presence of the calixarene in the mobile phase.

The K_A values and free Gibbs energies ΔG of the calixarene – aldehyde complexes are presented in Table.

As can be seen from Table, the stability constants (K_A = 57 M^{-1} – 1649 M^{-1}) strongly depend on the calixarene structure and the aromatic aldehyde nature. The enhancement of the complexing properties of calixarenes is observed in the row of **PRA** < **IC4A** < **PC4A** < **PC8A.** The volume of the calixarene molecular cavity plays the most important role in binding of aldehydes. **PC8A** exceeds **PRA, IC4A** and **PC4A** by 11-23 times for benzaldehyde, 6-15 times for salicylic aldehyde, 3-8 times for *p*-anisaldehyde, and 7-15 times for veratraldehyde complexation. It should be noted that the stability constant of the **IC4A** – benzaldehyde **1** complex (K_A = 146 M^{-1}) is close to those of the cyclophane – benzaldehyde complex (K_A = 120 M^{-1}) described in [22].

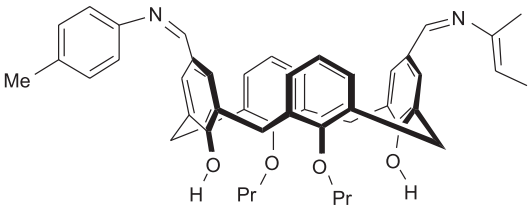
The calixarene Host-Guest complexes can be stabilized by hydrogen bonds, Van der Waals, π-π, C-H-π, and hydrophobic interactions. The role of the hydrophobic interaction is confirmed by the linear dependences of the binding constants K_A on the *log P* of aldehydes (Fig. 5).

The intermolecular hydrogen bonds between the Host and Guest molecules are clearly manifested in the energy

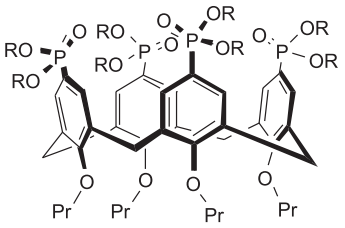


R = (O)P(OPh)$_2$

PRA

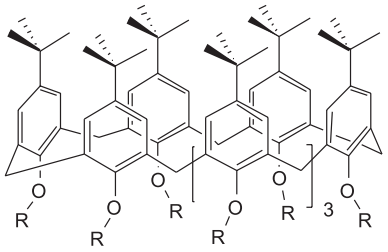


IC4A



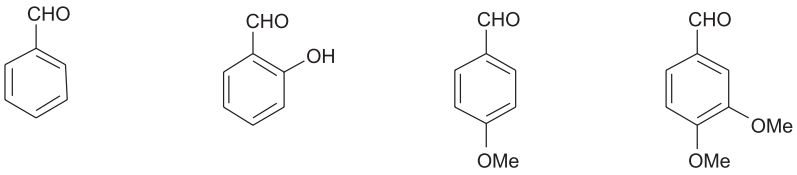
R=iPr

PC4A



R =(O)P(OEt)$_2$

PC8A



1 **2** **3** **4**

Scheme. Calix[4]arenes **PRA, IC4A, PC4A** and **PC8A** (Hosts), and benzaldehyde **1,** salicylaldehyde **2**, *p*-anisaldehyde **3** and veratraldehyde **4** (Guests)

minimized structures of the **IC4A, PC4A, PC8A** complexes with salicylaldehyde (Fig. 6). In the **IC4A** complex, the molecule of salicylaldehyde is included into the molecular cavity of the calixarene. In this case, the aldehyde hydroxyl group forms a hydrogen bond with the OH group oxygen atom on the lower rim of the macrocycle (O-H···O distance 2.84 Å).

In the inclusion complexes of **PC4A** and **PC8A** the salicylaldehyde OH group is associated with oxygen atoms of P=O groups located at the upper or the lo-

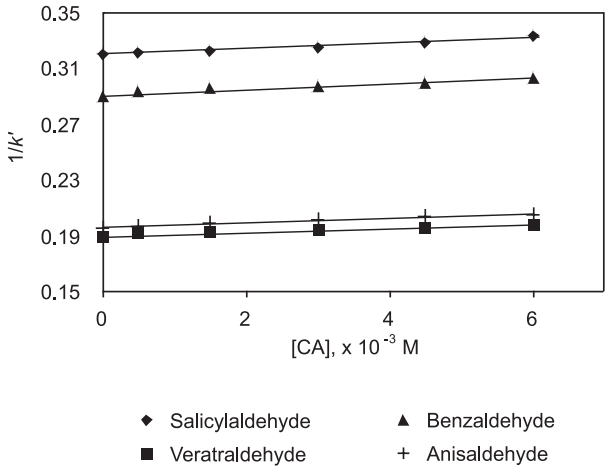


Fig. 1. Plots of 1/*k'* for aldehydes **1-4** *vs* the **PRA** concentration in the mobile phase (R^2 = 0.94-0.98)

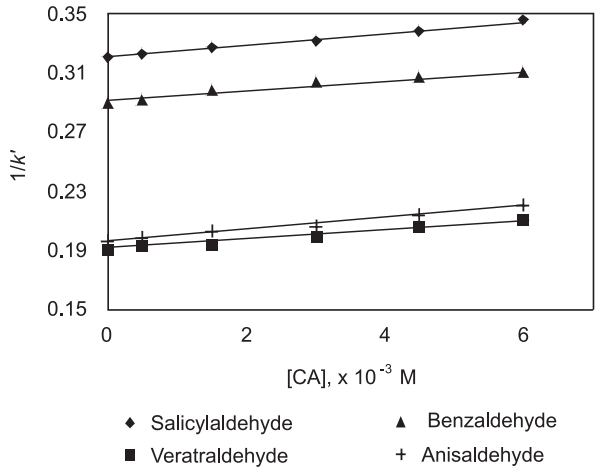


Fig. 2. Plots of 1/*k'* for aldehydes **1-4** *vs* the **IC4A** concentration in the mobile phase (R^2 = 0.96-0.99)

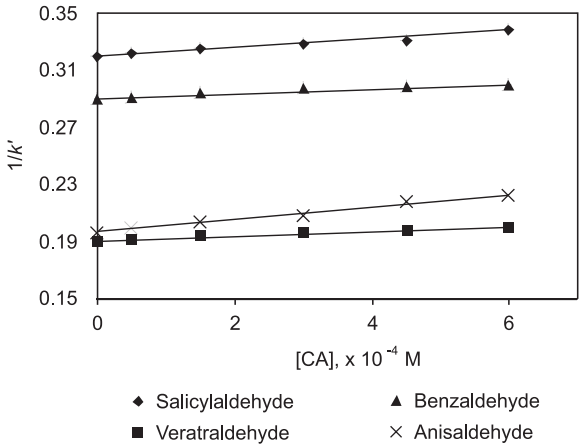


Fig. 3. Plots of 1/*k'* for aldehydes **1-4** *vs* the **PC4A** concentration in the mobile phase (R^2 = 0.95-0.99)

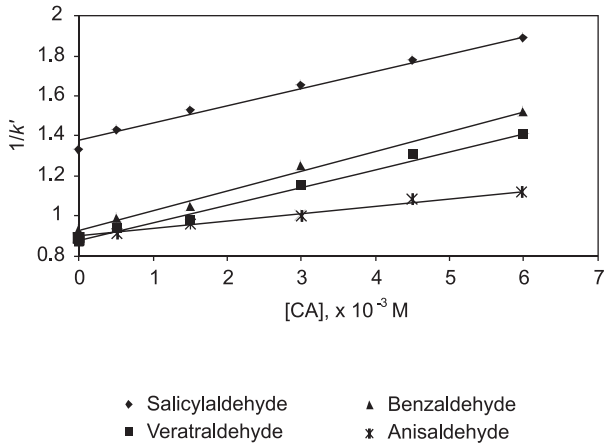


Fig. 4. Plots of 1/*k'* for aldehydes **1-4** *vs* the **PC8A** concentration in the mobile phase (R^2 = 0.97-0.99)

Table

The values of K_A (M^{-1}) and ΔG (kJ/mol) of the complexes **PRA**, **IC4A**, **PC4A,** and **PC8A** with aldehydes **1-4** (RSD = 8-20 %)

Aldehyde	PRA		IC4A		PC4A		PC8A	
	K_A	*DG*	K_A	*DG*	K_A	*DG*	K_A	*DG*
Benzaldehyde **1**	97	-11.32	146	-12.33	71	-10.54	1649	-18.32
Salicylaldehyde **2**	57	-10.0	142	-12.26	94	-11.24	858	-16.71
p-Anisaldehyde **3**	104	-11.49	195	-13.04	242	-13.58	797	-6.68
Veratraldehyde **4**	91	-11.16	179	-12.83	112	-11.67	1330	-17.79

wer rim of the macrocycle, respectively. The lengths of hydrogen bonds O-H···O=P are 2.38 Å for the **PC4A** complex and 2.87 Å for the **PC8A** complex.

As it is shown on Fig. 7, the experimental free Gibbs energies ΔG of calixarene complexes (Table) well correlate with relative energies $\Delta\Delta E$ of these complexes calculated by the molecular modeling method.

Experimental part

Calixarenes were synthesized by the methods early described: **PRA** [27], **IC4A** [28], **PC4A** [29] and **PC8A** [20]. Acetonitrile was obtained from Acros Organics (Thermo Fisher Scientific, New Jersey, USA) and aldehydes were purchased from Sigma-Aldrich (St. Louis, MO, USA).

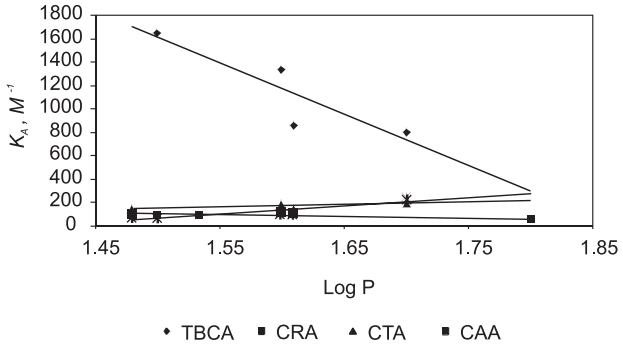


Fig. 5. Correlation of K_A of the calixarene complexes with *log P* of benzaldehyde **1** (1.50) [23], salicylaldehyde **2** (1.80) [24], *p*-anisaldehyde **3** (1.53) [25], veratraldehyde **4** (1.61) [26]. r = 0.94 (**PRA**), 0.73 (**IC4A**), 0.88 (**PC4A**) and 0.89 (**PC8A**)

RP HPLC analysis

The RP HPLC analysis was performed using the liquid chromatographic system (Hitachi, Ltd., Tokyo, Japan). The column (250 × 4.6 mm i.d.) was packed with LiChrosorb RP-18 (Merck, Darmstadt, Germany). Experiments were performed in isocratic conditions. The acetonitrile-water (80 : 20, v/v) mixture was used as a mobile phase. The calixarene concentrations in the mobile phases were 0.05-0.6 mM. The UV detector was operated at 254 nm, and the flow rate was

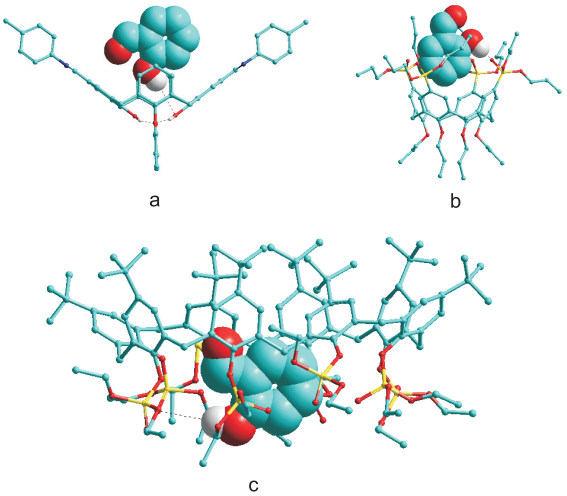


Fig. 6. The energy minimized structures of the Host-Guest complexes of salicylaldehyde with: **IC4A** (a), **PC4A** (b) and **PC8A** (c). Hydrogen bonds are shown as dotted lines

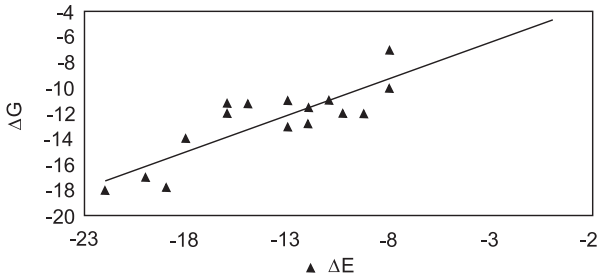


Fig. 7. Correlation of experimental values of free Gibbs energies ΔG of the calixarene complexes with relative energies ΔΔE of these complexes calculated by the molecular modeling method

0.8 ml/min. The samples of aldehydes for injections were dissolved in the same acetonitrile-water (80 : 20, v/v) mixture (C = 0.01 mM). All chromatograms were obtained at 26 °C. The mobile phase contained the calixarene additive was equilibrated for 3 h before the analysis. Under these conditions the LiChrosorb RP-18 column was saturated with the calixarene additive.

Molecular modeling

Molecular modeling of calixarene complexes was carried out using a Hyper Chem 8.0 program in the force field (PM3) [30]. The structures were calculated by the semi-empirical method. The RMS (standard deviation of the word root mean square) gradient was equal to 0.01 kcal/A mol.

Conclusions

Calix[4]arenes functionalized with two N-tolyliminomethyl groups or four diisopropoxyphosphonyl groups at the upper rim, calix[8]arene functionalized with eight diisopropoxyphosphoryl groups at the lower rim, and calix[4]resorcinarene functionalized with eight diphenoxyphosphoryl groups at the upper rim form the Host-Guest inclusion complexes with the aromatic aldehydes in acetonitrile-water solutions. The stability constants of the complexes (K_A = 57 M^{-1} – 1649 M^{-1}) strongly depend on the calixarene structure and the aromatic aldehyde nature. The enhancement of the complexing properties of calixarenes is observed in the row: **PRA < IC4A < PC4A < PC8A.** The Host-Guest complexation data can be used as a useful tool in design of calixarene based sensor devices for determination vapors of aldehydes in air or preparation of chromatographic phases for the analysis of aldehydes in solutions.

Conflict of interests: authors have no conflict of interests to declare.

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