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## Chromatographical study of alkyl-glucosides adsorption at solid-liquid interface

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Chromatographical study of alkyl-glucosides adsorption at solid-liquid interface from aqueous solutions were shown in this paper. The study of n-octyl- $\beta$ -D-glucopyranoside and n-decyl- $\beta$ -D-maltoside adsorption has been carried out on the mesoporous ordering silica SBA-15 using frontal and circulation chromatographical methods at 298 and 318 K.

As «proof of isotherms» a simple two-step adsorption model has been applied. The results of modeling show the reasonable values of the equation constants. Base on the isotherm analysis we try to figure out the conformation of surfactants species in pores. Thermodynamic parameters of surfactant adsorption at solid-liquid interface have been determined.

**Keywords:** Frontal and circulation chromatographical methods, two-step adsorption model, sugar-based surfactants, ordering silica SBA-15.

## Хроматографическое исследование адсорбции алкил-глюкозидов на границе твердое тело-жидкость

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В работе представлены результаты по исследованию адсорбции алкил-глюкозидов на границе твердое тело-жидкость. Изучение адсорбции н-октил-(beta)-D-глюкопиранозида и н-децил-(beta)-D-мальтозида на кремнеземе СБА-15 при двух температурах 273 и 318К, проводилось двумя хроматографическими методами: фронтальным и циркуляционным. Правильность экспериментальных данных была подтверждена двух-ступенчатой моделью процесса адсорбции. Результат моделирования отлично дополнил экспериментальные данные. Основываясь на экспериментальных данных была предложена модель упаковки мономеров ПАВ в слое сорбата на поверхности СБА-15. Так же, по экспериментальным данным, были рассчитаны термодинамические параметры процесса адсорбции.

**Ключевые слова:** фронтальная хроматография, циркуляционная хроматография, двухступенчатая модель адсорбции, глюкозосодержащие ПАВ, кремнезем СБА-15

### Introduction

The global output of surfactants increases with the corresponding increase in the need for greener surfactants during past years [1-3]. The major part of the surfactants currently produced is used as cleaning and washing agents. The key process for utilization of surfactants is a further purification of waste solution to reduce the impact on the environmental. It is not surprising that recently scientists have focused on the

investigations of «waste water treatment». Sugar-based surfactants are biodegradable, nontoxic, compatible with environment and producible from renewable materials, and so they have drawn a great deal of attentions as a new generation of nonionic surfactants [4-8].

For purification and evolution of surfactants in waste water, high selectivity and capacity of porous materials is often needed to separate these molecules from mixtures or multi-component solutions containing impurities with similar chemical properties. Mesoporous silica materials such as SBA-1, SBA-15 and SBA-16 have been the subject of much interest since they have been reported by researchers. SBA-15 silica has a hexagonal structural array of unidirectional pores. The synthesis and utilization of these materials have been investigated by many researchers because of their special characteristics such as highly regular pore structure, uniform pore size, high surface area ( $\sim 1000 \text{ m}^2 \text{ g}^{-1}$  and above) and high thermal stability. Various physico-chemical methods and modern liquid chromatography have been successfully used for a comprehensive study of the properties of these sorbents [9-16].

Previously [13, 14] chromatographical studies have been carried out on the investigation the features of liquid-solid adsorption of alkyl-polyethylene oxides ( $C_mE_n$ ) on mesoporous silica material SBA-15.

Here we study by frontal and circulation chromatographical methods the behavior of n-octyl- $\beta$ -D-glucopyranoside ( $C_8G_1$ ) and n-decyl- $\beta$ -D-maltoside ( $C_{10}G_2$ ) at solid-liquid interface - as a model of biocompatible and environmentally friendly surfactants under key operating conditions, such as temperature and concentration. In addition we study the lateral structure of the adsorbed layer of  $C_mG_n$  surfactants in mesoporous space of silica SBA-15 by analyzing of adsorption isotherms and molecular structure of sugar-based surfactants.

## Experimental

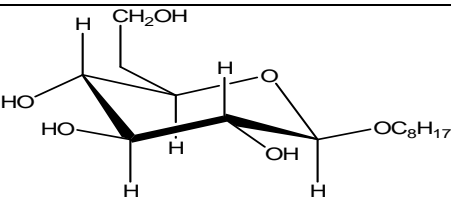
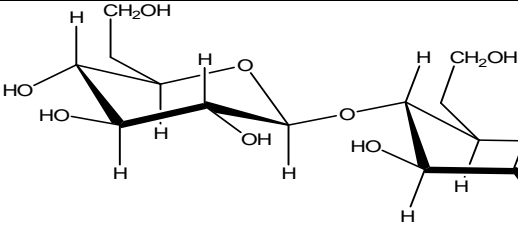
We used two nonionic sugar-based surfactants: n-octyl- $\beta$ -D-glucopyranoside and n-decyl- $\beta$ -D-glucomaltoside (see Table 1). Both the surfactants have been obtained from Fluka Inc. (Berlin, Germany) and were used without further purification. Deionized water was purified by a Milli-Q Water Purification System (Millipore, Bedford, USA). All surfactant solutions were prepared by dissolving individual surfactant or a stock surfactant solution in deionized water. The resulting mixtures were sonicated for ca. 15 min at 298 K.

SBA-15 was synthesized in our laboratory as reported in [9, 11, 16]. As proof of silica material quality the nitrogen adsorption on the synthesized silica SBA-15 has been measured at 77 K by using Gemini 2375 automatic analyzer (Micromeritics, USA). Specific surface area and average pore size were determined by *BET* and *BJH* methods from the adsorption isotherm branch. Nitrogen adsorption isotherm for SBA-15 is characterized by the *H*-type hysteresis. Such isotherm form is mainly due to high mesoporosity of adsorbent [11, 16]. The surface area of synthesized SBA-15 was  $740 \text{ m}^2 \text{ g}^{-1}$ , the average pore size was 6.6 nm and the pore volume was about  $0.96 \text{ cm}^3 \text{ g}^{-1}$ .

Currently various chromatographical methods are widely used for physico-chemical investigations of the processes at the interface [13, 14, 17-25]. Here we apply frontal (FA) and circulation (CA) chromatographical methods to study the adsorption interaction of sugar-based surfactants with synthesized SBA-15. We used the same chromatographical installation for both of liquid chromatographical methods. The chromatographical installation consists of chromatographic pump K-1001 (Knauer, Germany), a selection valve, degasser manager 5000 (Knauer, Germany), differential

refractive index detector K 2301 (Knauer, Germany), a liquid flow meter, chromatographic column (20mmx4 mm) packed with SBA-15 silica, interface box and PC with EuroChrom 2000 software running under MS Windows (Knauer, Germany).

Table 1. Chemical properties of surfactants with molecular weight ( $M_w$ ) and critical micelle concentration (CMC) values

Surfactant	Mol. structure	$M_w$	CMC, $\text{mmol L}^{-1}$
n-octyl- $\beta$ -D-glucopyranoside		292.4	22
n-decyl- $\beta$ -D-glucomaltoside		440.5	2.0

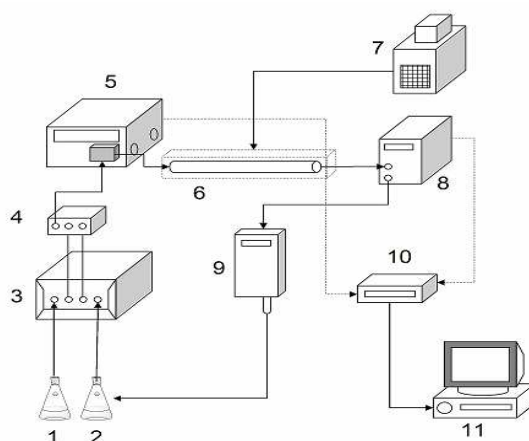


Fig. 1. Chromatographical installation: 1-Solute, 2-Solvent, 3-Degassing unit, 4-Mixing chamber, 5-Pump, 6-Column, 7-Thermostat unit, 8-RI detector, 9-Flow meter, 10-Readout unit, 11-Personal computer

The chromatographical column was packed with SBA-15 by packing equipment (Alltech, Model 1666, U.S.) at 550 bar. For all experiments column were thermostated at 298 and 318 K, respectively. The eluent was prepared by deionized distillate water. The void volume ( $V_o$ ) was estimated by passing 2%  $D_2O$  in pure water solution through the chromatographical system and measuring the retention time of  $D_2O$ . The error for  $V_o$  was less than  $\pm 0.3\%$ .

Frontal chromatographical method has been applied particularly for adsorption from dilute solution ( $0.1-0.2 \times \text{CMC}$ ) to avoid using a large volume of surfactant for solution (Fig. 2). The column was packed with SBA-15 and the measurements of the adsorbed amount were made of difference between the retention volumes of surfactant and  $D_2O$  and the concentrations of ingoing and outgoing solutions from column. The difference

between them has been monitored by RI detector. In FA method the errors of determination of the retention volume and equilibrium concentration of surfactants in bulk solution were estimated approximately as 2.5 and 0.8%, respectively.

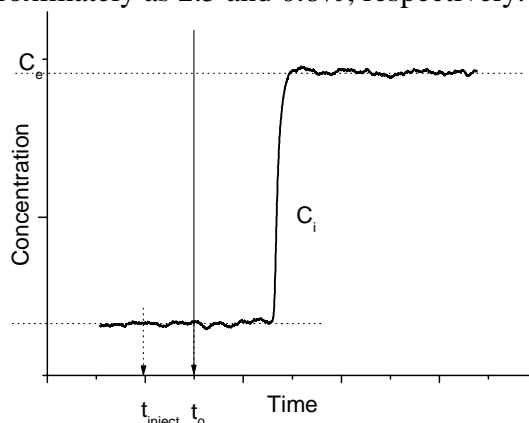


Fig. 2. Outlet curve in FA method:  $t_{inject}$  - inject time,  $t_0$  - retention time of  $D_2O$ ,  $C_e$  and  $C_i$  - equilibrium and current concentrations

The value of excess adsorbed amount  $\Gamma$  for surfactant in FA method was calculated as following [14]

$$\Gamma = \frac{w}{A} \int_{t_0}^{t_{\infty}} (C_e - C_i) dt \quad (1)$$

where  $w$  is the flow rate of the mobile phase,  $A$  is the surface area of the adsorbent in the column,  $C_e$  and  $C_i$  are the equilibrium concentration and the concentration at the moment ( $t$ ), respectively,  $t_0$  is the retention time of  $D_2O$ ,  $t_{\infty}$  is the time when  $C_i$  achieves same value as  $C_e$ .

In a region of concentrated solutions (above  $0.2 \times CMC$ ) we apply a circulation chromatographical method [23], where a chromatographic equilibrium was achieved by circulation of solution over the column with SBA-15. The concentration of the surfactants in solution was monitored continuously by RI detector (Fig. 3). For CA method the corresponding errors in the estimating of the corrected retention volume and the equilibrium concentration were less than 0.8 and 0.5%, respectively.

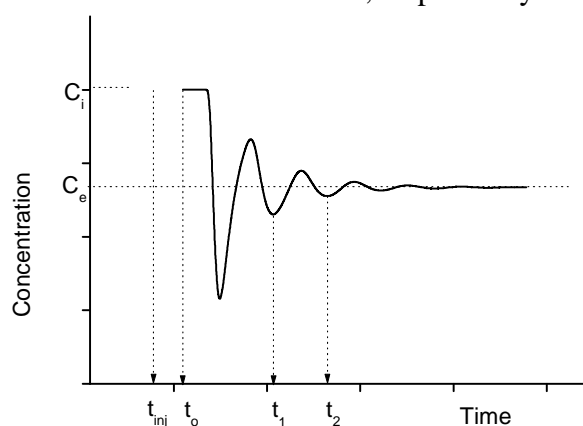


Fig. 3. Outlet curve in CA method:  $t_{inj}$  - inject time,  $t_0$  - retention time of  $D_2O$ ,  $t_1$  and  $t_2$  - times of retention in the first and second cycles, respectively,  $C_i$  and  $C_e$  - initial and equilibrium concentrations, respectively.

The value of excess adsorbed amount  $\Gamma$  for surfactant in CA method was calculated as following [14]

$$\Gamma(C_N) = \frac{1}{AN} \sum_1^N (C_i - C_e) V_R \quad (2)$$

where  $N$  is a number of cycle,  $C_i$  and  $C_e$  – initial and equilibrium concentrations,  $V_R$  is a corrected retention volume.

## Results and discussion

The isotherms of  $C_8G_1$  and  $C_{10}G_2$  adsorption from aqueous solutions on silica SBA-15 were obtained by chromatographical method for two temperatures (Fig. 4AB, 5AB). These isotherms are characterized by the linear initial parts in a region of low concentrations (Fig. 4B, 5B). At the same time, with increasing of the concentration isotherms of n-alkyl-glucosides show sharp rise and finally reach a plateau at the concentration slightly above CMC of given surfactant in the bulk solution. Similar isotherms can belong to the LS-type isotherms (Fig. 4A, 5A).

Fig. 4B and 5B presents the initial parts of surfactants  $C_8G_1$  and  $C_{10}G_2$  adsorption isotherms on silica SBA-15. These parts of adsorption isotherms can be described with the Henry equation because of the lineal forms.

From the experimental corrected retention volume  $V_R$  we can obtain the meaning of  $K_H$  - Henry constant as [14, 18, 21, 25]

$$K_H = V_R / A \quad (3)$$

where  $A$  is the surface area of the packing material in chromatographical column.

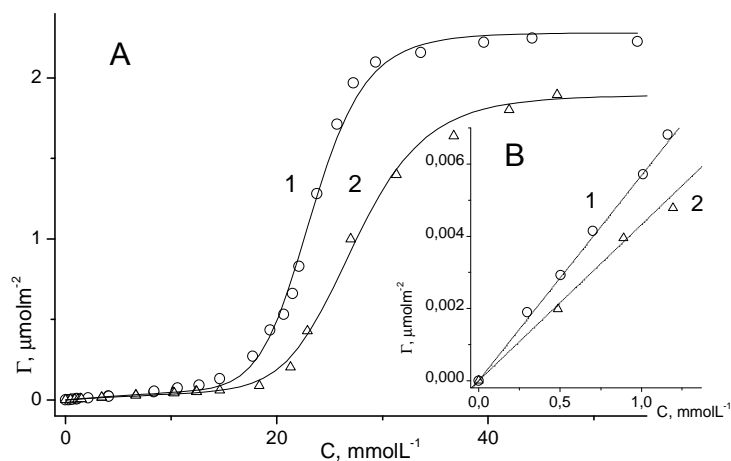


Fig. 4. Adsorption isotherms of  $C_8G_1$  (A) from aqueous solutions in SBA-15 silica at 298 K (1) and 318 K (2). Points – chromatographical data, solid curves – modeling isotherms with Eq. 5. Initial part of adsorption isotherms of  $C_8G_1$  (B) from aqueous solutions in SBA-15 silica at 298 K (1) and 318 K (2). Points – chromatographical data, dot line - fit linear.

The expression for the change of the  $\Delta G^o$  - free Gibbs energy in the adsorption process for  $C \rightarrow 0$  is found enough simple

$$\Delta G^o = RT \ln(K_H / K_H^o) \quad (4)$$

where  $K_H^o$  is the constant for standard state equal to  $1 \text{ mm}^3/\text{m}^2$  [14, 21, 22, 25].

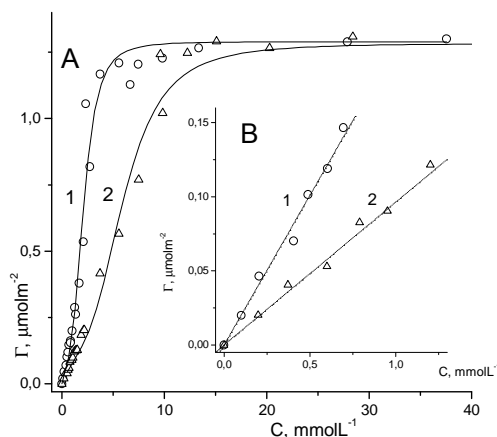


Fig. 5. Adsorption isotherms of C10G2 (A) from aqueous solutions in SBA-15 silica at 298 K (1) and 318 K (2). Points – chromatographic data, curves – modeling isotherms with Eq. 5. Initial part of adsorption isotherms of C10G2 (B) from aqueous solutions in SBA-15 silica at 298 K (1) and 318 K (2). Points – chromatographic data, dot line - fit linear.

From the temperature dependences of the  $\Delta G^\circ$  we can estimate the value of  $\Delta H^\circ$  – change of displacement enthalpy. Chromatographical data and calculated thermodynamic parameters have been shown in Table 2.

Table 2. Retention volumes  $V_R$  (ml) and thermodynamic quantities for adsorption of surfactants  $C_8G_1$  and  $C_{10}G_2$  on Silica SBA-15

Surfactant	Temperature, K	$V_R$ , ml	$K_H^\circ$ , $\text{mm}^3/\text{m}^2$	$\Delta G^\circ$ , kJ/mol	$\Delta H^\circ$ , kJ/mol
n- $C_8G_1$	298	0.22	5.8	-4.4	-11.2
	318	0.16	4.4	-3.9	
n- $C_{10}G_2$	298	7.0	190	-12.9	-27.3
	318	3.5	94	-11.0	

The values of  $V_R$ ,  $K_H^\circ$ ,  $\Delta G^\circ$  and  $\Delta H^\circ$  become significantly large for surfactant  $C_{10}G_2$  in comparison with  $C_8G_1$ . However the meanings of  $\Delta G^\circ$  exhibit a weak temperature dependence of  $C_8G_1$  and  $C_{10}G_2$  and were determined only at two temperatures. There are also the elements of uncertainty in the values of  $\Delta H^\circ$ .

The thermodynamic quantity summarized in the Table 2 shows that the addition of two  $\text{CH}_2$ -groups in alkyl chain and one glucoside unit in surfactant  $C_8G_1$  molecule leads to marked enhancement of  $V_R$ ,  $K_H^\circ$  and the thermodynamic quantities for n-alkyl-glucosides adsorption on mesoporous silica SBA-15 walls. Here we can compare the enthalpies of monolayer formation for surfactant  $C_8G_1$  on Silica SBA-15 and Silica porous glass CPG10-240 [13, 14] to be  $\Delta H^\circ = -11.2$  and  $\Delta H^\circ = -8.1 \text{ kJmol}^{-1}$ , respectively. A little difference in these values is due to the effect of adsorption potential strengthening in the narrow channels of the silica SBA-15. The enthalpies of monolayer formation for  $C_8G_1$  on the hydrophobic graphitized carbon to be  $\Delta H^\circ = -26 \text{ kJmol}^{-1}$  [11, 13] is very high in the comparison with one on the silica SBA-15.

As shown in Fig. 4A and 5A the maximum adsorption capacity ( $\Gamma_\infty$ ) of C8G1 on SBA-15 are equal  $2.3 \mu\text{mol m}^{-2}$  and  $1.9 \mu\text{mol m}^{-2}$  at 298 and 318 K, respectively. Increasing in molecular weight of surfactant by two hydrocarbon  $\text{CH}_2$ -groups and one glucose unit leads to decreasing of  $\Gamma_\infty$  and yields for C<sub>10</sub>G<sub>2</sub> on SBA-15  $\Gamma_\infty = 1.3 \mu\text{mol m}^{-2}$  at 298 K. At the equilibrium concentration closed to CMC the temperature effect on the aggregate formation from the molecules C<sub>10</sub>G<sub>2</sub> is very small.

The temperature change, however, shows a typical effect on adsorption, i.e. with increase of temperature adsorption decreases, while for n-alkyl poly(ethyleneglycol) ethers (C<sub>m</sub>E<sub>n</sub>) we observe an opposite effect [13, 14], although both surfactants, C<sub>m</sub>G<sub>n</sub> and C<sub>m</sub>E<sub>n</sub>, belong to the class of nonionic surfactants. The explanation is, perhaps, that the head groups of C<sub>m</sub>E<sub>n</sub> surfactant molecule undergo strong dehydration along increasing temperature and therefore whole molecule is adsorbing more strongly. This also explains why the  $\Gamma_\infty$  for C<sub>m</sub>E<sub>n</sub> surfactants on SBA-15 is much higher than that for C<sub>m</sub>G<sub>n</sub>. In case of C<sub>m</sub>G<sub>n</sub> adsorption the glucose head group is less sensitive towards temperature changes and keeps constant its hydration ratio in this temperature range.

Here we used the modified isotherm equation for two-step adsorption model to describe the process of n-alkylglucoside adsorption from aqueous solutions on mesoporous silica SBA-15 as following [5, 14]:

$$\Gamma = \Gamma_\infty \frac{k_1 C_o^n + C^n}{nC_o^n + nk_1 C_o^n C + C^n} \quad (5)$$

where  $\Gamma$  and  $\Gamma_\infty$  are the amount of adsorbed surfactant at the concentration  $C$  and the total amount of adsorbed surfactant, respectively,  $C_o$  is the critical surface aggregation concentration,  $k_1$  is the equilibrium constant for the first step of adsorption process and  $n$  is the number of surfactant molecules in micelle (aggregation number).

As evident from Fig. 4A, 5A the two-step adsorption model fits well the experimental data and the satisfactory correlation between the modeling on Eq. 5 curves and the measured n-alkyl-glucoside adsorption isotherms have been observed. The calculated parameters of n-alkyl-glucoside adsorption on SBA-15 using Eq. 5 have been done in Table 3.

Table 3. Application of Eq. 5 for n-alkyl-glucoside adsorption isotherms on silica SBA-15 from aqueous solutions

Surfactant	T, K	$\Gamma_\infty$ , $\mu\text{molm}^{-2}$	$C_o$ , $\text{mmol L}^{-1}$	$n$
n-C <sub>8</sub> G <sub>1</sub>	298	2.3	17.9	10.8
	318	1.9	20.3	8.5
n-C <sub>10</sub> G <sub>2</sub>	298	1.3	1.3	3.9
	318	1.3	3.4	4.5

As it is seen from Table 3 the increasing of the surfactant molecular size leads to the decrease of the adsorption amount,  $\Gamma_\infty$ , and the aggregation number  $n$ . The surfactant molecules C<sub>10</sub>G<sub>2</sub> form the aggregates with  $n = 4-5$ .

## Conclusion

For the first time the study of sugar-based surfactants n-octyl- $\beta$ -D-glucopyranoside and n-decyl- $\beta$ -D-maltoside adsorption has been carried out on the mesoporous ordering silica SBA-15 with frontal and circulation variants of HPLC method at 298 and 318 K.

From the retention volumes of studied sugar-based surfactants the thermodynamic quantities – the Gibbs energy and the displacement enthalpy have been determined.

For the description of the behavior of n-alkyl-glucoside molecules at the liquid-solid interface we have applied isotherm equation for two-step adsorption model. The obtained values of aggregation number indicate on the formation of adsorbed aggregates of small sizes at the concentration of sugar-based surfactants closed to the CMC. At the low concentration of sugar-based surfactants the separate molecules are adsorbing and form the monolayer.

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