



Original article

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## Kinetic features of the adsorption of menthol enantiomers on *o*-toluic acid and CsCuCl<sub>3</sub> crystals with supramolecular chirality

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**Abstract.** Chirality plays a key role in modern science because it is the distinguishing feature of molecules and crystals. The spontaneous emergence of chirality in the absence of detectable chiral physical and chemical sources has recently advanced significantly due to the deracemization of conglomerates through Viedma ripening. As a result, systems based on supramolecular chirality are obtained. Of particular importance to this type of chirality is the fact that supramolecular chirality underlies the formation of life on Earth. One manifestation of supramolecular chirality is enantiomorphic crystals.

Previously, we studied the mechanism of supramolecular chiral recognition for enantiomorphic crystals in the case of adsorption of optically active substances on them. However, for a more detailed study of the mechanism, it is required to study a large number of chiral crystals, which differ in their physicochemical properties. In this work, we studied the adsorption kinetics of menthol enantiomers on the surface of enantiomorphic crystals of *o*-toluic acid and CsCuCl<sub>3</sub> with supramolecular chirality.

The Viedma ripening method was used to obtain homochiral crystals. The crystals obtained in this way were deposited on the surface of the ASKG silica gel. The kinetics of adsorption has been studied by describing chemical models of Lagergren's pseudo-first order, Ho and McKay's pseudo-second order, and the Elovich model, simplified by Chen and Clayton. Boyd model of film diffusion and Weber-Morris and Dumwald-Wagner models dealing with intraparticle diffusion were used as well.

From an analysis of the adsorption curves of menthol enantiomers, it is noticeable that the curves differ on the crystals under consideration. The enantioselectivity coefficient on crystals of *o*-toluic acid and CsCuCl<sub>3</sub>  $\alpha$ , calculated as the ratio of higher adsorption to lower one, is 1.04-1.07 and 1.34-1.36 respectively. Using the *t*-test, the adsorption values of menthol enantiomers on enantiomorphic crystals of *o*-toluic acid and CsCuCl<sub>3</sub> were processed until equilibrium was reached. The variances of all experimental data were checked for homogeneity using the *F*-test. It follows from the obtained data that the difference in adsorption values is statistically significant for the sample modified with both *o*-toluic acid and CsCuCl<sub>3</sub>.

Based on the results obtained in the process of modeling the adsorption kinetics of menthol enantiomers by chemical models, the adsorption rate constants were calculated. It was found that in all methods the rate constants of D-menthol and L-menthol are different, and D-menthol is adsorbed faster than L-. From the data obtained, it is noticeable that the adsorption equilibrium in the case of both samples is shifted to the right.

Thus, the difference in adsorption rate constants, as well as significant differences in the adsorption values of enantiomers in the region until adsorption-desorption equilibrium is reached, indicates that the adsorption rate of menthol enantiomers on crystals of *o*-toluic acid and CsCuCl<sub>3</sub> obtained under Viedma ripening conditions is different.

**Keywords:** *o*-toluic acid, CsCuCl<sub>3</sub>, Viedma ripening, chiral recognition, supramolecular chirality, adsorption kinetic.

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## ОРИГИНАЛЬНЫЕ СТАТЬИ

Научная статья

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### Кинетические особенности адсорбции энантиомеров ментола на кристаллах орто-толуиловой кислоты и $\text{CsCuCl}_3$ с супрамолекулярной хиральностью

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**Аннотация.** Хиральность играет ключевую роль в современной науке, поскольку она представляет собой отличительную особенность молекул и кристаллов. Самопроизвольное появление хиральности в отсутствие обнаруживаемых хиральных физических и химических источников в последнее время значительно продвинулось вперед благодаря дерацемизации конгломератов посредством созревания Виедмы. В результате этого получают системы, основанные на супрамолекулярной хиральности. Особую важность данному виду хиральности придает то, что супрамолекулярная хиральность лежит в основе формирования жизни на Земле. Одним из проявлений супрамолекулярной хиральности являются энантиоморфные кристаллы.

Ранее нами был изучен механизм супрамолекулярного хирального распознавания для энантиоморфных кристаллов в случае адсорбции на них оптически активных веществ. Однако, для более детального изучения механизма, требуется исследовать большое количество хиральных кристаллов, которые отличаются по физико-химическим свойствам. В данной работе изучена кинетика адсорбции энантиомеров ментола на поверхности энантиоморфных кристаллов о-толуиловой кислоты и  $\text{CsCuCl}_3$  с супрамолекулярной хиральностью.

Для получения гомохиральных кристаллов применялся метод созревания Виедмы. Кристаллы, полученные таким образом были нанесены на поверхность силикагеля АСКГ. Кинетика адсорбции изучалась описанием химическими моделями псевдо-первого порядка Лагергрена, псевдо-второго порядка Хо и Маккея, а также модель Еловича, упрощенное Ченом и Клейтоном. Также применялись диффузионные уравнения Вебера-Морриса, Бойда и Думвальда-Вагнера.

Из анализа кривых адсорбции энантиомеров ментола заметно, что кривые различаются на рассматриваемых кристаллах. Коэффициент энантиоселективности на кристаллах о-толуиловой кислоты и  $\text{CsCuCl}_3$   $\alpha$ , рассчитываемый как отношение большей адсорбции к меньшей, составляет 1.04-1.07 и 1.34-1.36 соответственно. С помощью t-критерия были обработаны значения адсорбции энантиомеров ментола на энантиоморфных кристаллах о-толуиловой кислоты и  $\text{CsCuCl}_3$  до достижения равновесия. Дисперсии всех экспериментальных данных проверялись на предмет однородности с помощью F-критерия. Из полученных данных следует, что различие значений адсорбции статистически значимо на образце, модифицированном как о-толуиловой кислотой, так и  $\text{CsCuCl}_3$ .

По результатам, полученных в процессе моделирования кинетики адсорбции энантиомеров ментола химическими моделями, вычислили константы скорости адсорбции. Было установлено, что во всех методах константы скорости D-ментола и L-ментола различаются, причем D-ментол адсорбируется быстрее, чем L-. Из полученных данных заметно, что адсорбционное равновесие в случае обоих образцов смещено вправо.

Таким образом, различие констант скорости адсорбции, а также значимые отличия значений адсорбции энантиомеров в области до достижения адсорбционно-десорбционного равновесия свидетельствует о том, что скорость адсорбции энантиомеров ментола на полученных в условиях созревания Виедмы кристаллах о-толуиловой кислоты и  $\text{CsCuCl}_3$  различна.

**Ключевые слова:** о-толуиловая кислота,  $\text{CsCuCl}_3$ , созревание Виедмы, кривые адсорбции, хиральное распознавание, супрамолекулярная хиральность, модель псевдо-первого порядка Лагергрена, модель псевдо-второго порядка Хо и Маккея, модель Еловича, модель Бойда, модель Вебера-Морриса, модель Думвальда-Вагнера.



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## Introduction

Chirality is an inherent property of natural materials, including minerals, organic molecules, and biological structures. Chirality can be identified both in molecules and in supramolecular formations, such as crystals [1]. Pasteur was the first, who noticed the analogy between crystals and molecules in this context. He realized that the non-identity of a crystal (or a molecule) with its own specular reflection is due to what he called dissymmetry. It is known that the two enantiomers differ in their physiological effects: one enantiomer may be an effective drug, while the other may be toxic. Therefore, the development of new methods for chiral recognition and separation of optical isomers is of practical importance for drugs and biologically active compounds design. In chromatography, in the most cases, enantiomers are separated by interaction with a chiral selector, which is either fixed to a solid substrate or added to the mobile phase. As a result of the interaction, diastereomeric complexes are formed between the enantiomers of the analyzed substance and the chiral selector. They differ in physical and chemical characteristics. Due to this approach, more than 50 years ago Davankov [2, 3] and Gil-Av [4] performed the first chromatographic separations of enantiomers. Enantioselective stationary phases based on cyclodextrins have been used in gas chromatography for several decades. Cyclodextrins occupy a leading position in chiral GC, but many challenges require more selective chiral stationary phases.

In this context, concepts based on supramolecular chirality were tempting. Supramolecular chirality implies a dissymmetric arrangement of molecular components in a non-covalent assembly. Elements with this type of chirality can be obtained as a result

of a certain spatial arrangement of molecules [5]. In this case, they have higher levels of hierarchy than simple molecules – they consist of several layers of molecules or atoms. Chiral supramolecular structures can be formed from both chiral and achiral molecules. The latter can be used either in the case of an external source of chirality, or by spontaneous violation of chiral equilibrium. Enantiomorphic crystals are the examples of elements with supramolecular chirality. These objects is usually obtained by crystallization of optically pure substances [6]. However, in some cases optically pure crystals can also be obtained from molecular achiral compounds. Such crystals are suitable for studying the effect of supramolecular chiral recognition, because there is no effect of chiral molecular recognition.

Among a lot of methods for obtaining individual enantiopure crystals from a racemic or achiral solution, the method of Viedma ripening has shown the greatest reliability. In this process, the ratio of the crystallization centers of the two optical forms is disrupted by continuous grinding of the suspension. Further, the Frank autocatalytic process leads to a complete shift in the chiral equilibrium: the crystals of one of the enantiomorphs completely dissolve and the other enantiomorph crystallizes.

Previously, Viedma ripening was successfully applied to obtain enantiomorphic crystals of achiral molecules. These crystals were studied for their ability to recognize enantiomers in adsorption processes. It was found that the chiral recognition of enantiomers was caused by different energies of lateral interactions of adsorbate on the crystal surface. So there was a difference in the thermodynamic characteristics of the adsorption of enantiomers. However, it was previously determined that the Van Deemter curves for optical isomers have differed. Therefore,

there may also be differences in the rate of adsorption of enantiomers. However, this phenomenon has not been thoroughly studied.

In this paper, the kinetics of menthol enantiomers adsorption on *o*-toluic acid and CsCuCl<sub>3</sub> crystals with supramolecular chirality was studied. Various models have been used to describe kinetic curves, such as Lagergren's pseudo-first-order model, Ho and McKay's pseudo-second-order model, and the Elovich model simplified by Chen and Clayton. Boyd model of film diffusion [12] and Weber-Morris [13] and Dumwald-Wagner [14] models dealing with intraparticle diffusion were used as well.

### Experimental part

*o*-Toluic acid crystals (99%, Sigma Aldrich, China, CAS No. 118-90-1) and CsCuCl<sub>3</sub> were selected as the compounds for crystallization. The latter were obtained by the reaction of CuCl<sub>2</sub> (>99%, Reachim, St. Petersburg, Russia, 7447-39-4) and CsCl (>99%, Reachim, St. Petersburg, Russia, 7647-17-8)

To obtain homochiral crystals, the method of Viedma ripening was used. To obtain enantiopure crystals of *o*-toluic acid, 17 g of *o*-toluic acid were dissolved in 160 ml of acetonitrile. 9 g of glass beads were added to create a "mill" effect. The resulting suspension was stirred at a speed of 1000 rpm for 2 hours, and then left to ripe for two days [7].

To obtain CsCuCl<sub>3</sub> crystals, a saturated solution containing 57.2 g of CsCl in acidified water was gradually added to a solution containing 110.8 g of CuCl<sub>2</sub> at 32 °C (pH=1.39). The resulting solution was intensively stirred in the presence of glass beads at a speed of 1300 rpm. Then the temperature was reduced to room temperature and stirring was continued for 2 days. The solution was left for 7 days in an open flask to complete the autocatalytic process. The suspension was filtered, and the resulting precipitate was dried in a desiccator over CaCl<sub>2</sub> for a day. After that, the adsorbent was additionally dried in a nitrogen stream for an hour.

As a result, crystals of a characteristic garnet-black color were obtained.

The specific surface area of the crystals is several m<sup>2</sup>/g. For this reason, the value of adsorption on crystals is too small for reliable chiral discrimination determination. Therefore, to increase the specific surface area, the obtained crystals were applied on the surface of ASKG silica gel (Reachim, St. Petersburg, Russia, CAS No. 112926-00-8). To apply *o*-toluic acid, 220 ml of acetonitrile and 10 g of crystals were added to 50 g of ASKG silica gel. The suspension was stirred for 2 hours, and then the precipitate was filtered and dried. To apply CsCuCl<sub>3</sub> crystals, a saturated solution of CsCl in acidified water was gradually added to the CuCl<sub>2</sub> solution with continuous stirring (pH=1.39). 5 g of previously obtained CsCuCl<sub>3</sub> crystals were added to the solution, then stirred for 30 minutes. Then 50 g of silica gel was added. The stirred solution was evaporated at room temperature until stirring became impossible.

The adsorption of menthol enantiomers from solutions was studied using the following algorithm. A 0.5 g silica gel sample modified with *o*-toluic acid or CsCuCl<sub>3</sub> was added to a solution of D- or L-menthol in *n*-heptane. The volume of the solution was 20 ml. The concentration of menthol in the case of studying the adsorption activity of *o*-toluic acid was 70 µg / ml; for CsCuCl<sub>3</sub> – 220 µg/ml. The choice of menthol concentrations was determined by the analysis of previously obtained data [8]. The concentration was chosen when the difference in the adsorption of enantiomers by modified enantiomorphous silica gel crystals was maximal. The volume of the analyzed substance was 5 µl. To obtain kinetic adsorption curves, samples were taken after adding the sorbent for certain periods of time.

The amount of the adsorbed substance was determined using a Crystall-5000.2 gas chromatograph with a flame ionization detector with an SBP-1 capillary column measuring 30m·0.53mm. The temperature of the evaporator and detector was 220 °C. The adsorbed substances were D-menthol (99%,



Sigma Aldrich, Germany, CAS No. 15356-60-2) and L-menthol (99%, Sigma Aldrich, China, CAS No. 2216-51-5).

The equilibrium adsorption value ( $a$ ,  $\mu\text{mol/g}$ ) was calculated as follows:

$$a = \frac{(c_0 - c_x)V}{Mm}, \quad (1)$$

where  $c_0$  was the concentration before adsorption of  $\mu\text{g/ml}$ ;  $c_x$  was the concentration after adsorption,  $\mu\text{g/ml}$ ;  $V$  was n-heptane volume, ml,  $M$  was the molecular weight of menthol, g/mol, and  $m$  is the mass of the adsorbent. The relative standard deviation for adsorption values did not exceed: on CsCuCl<sub>3</sub> for L-menthol – 2.3%, for D-menthol – 3.3%, on o-toluic acid for L-menthol – 4.6%, for D-menthol – 9.8%.

The kinetic curves were approximated using pseudo-first-order Lagergren, pseudo-second-order Ho and McKay models, as well as the Elovich model, as well as Boyd, Weber-Morris and Dumwald-Wagner diffusion models.

The pseudo-first-order Lagergrenian equation in linear form looks like this [9]:

$$\ln(a_e - a) = \ln a_e - k_1 t, \quad (2)$$

where  $a_e$  was the adsorption value when the adsorption equilibrium was reached,  $a$  was the adsorption value at time  $t$ , and  $k_1$  was the pseudo-first-order rate constant,  $\text{min}^{-1}$ . From a physicochemical point of view, a pseudo-first-order model will describe experimental data only if the adsorption is limited by the transport of molecules from solution to adsorbent. This is because the model describes cases of film diffusion, which controls the rate of adsorption during the first few minutes in experiments with mixing [10].

The pseudo-second-order equation of Ho and McKay [11] in the integrated form, can be calculated as follows [12]:

$$\frac{t}{a} = \frac{1}{k_2 a_e^2} + \frac{t}{a_e} \quad (3)$$

where  $k_2$  is the pseudo-second-order adsorption rate constant,  $\text{g}/(\mu\text{mol}\cdot\text{min})$ .

This equation allows us to consider not only the sorbate-sorbent interactions, but also the intermolecular interactions of the adsorbed substances, which determines the

high adequacy of using the kinetic model of Ho and McKay.

The Elovich equation is often used to describe the kinetics of adsorption of substances in heterogeneous systems, with considering the sorption capacity. The Elovich equation simplified by Chen and Clayton [13], has the following form:

$$a = \frac{1}{\beta} \cdot \ln(\alpha \cdot \beta) + \frac{1}{\beta} \ln t, \quad (4)$$

where  $\alpha$  was the initial adsorption rate constant,  $\mu\text{mol}/(\text{g}\cdot\text{min})$ ;  $\beta$  was the desorption constant,  $\mu\text{mol/g}$ .

This equation was previously successfully used to describe the chemisorption of gas molecules on a sorbent. A general explanation of this form of kinetic law involves a change in the chemisorption energy depending on the surface coverage. But in recent years this equation has been widely used to describe the kinetics of gas adsorption by solids [20].

For the primary distinction between intra- and external diffusion limitation of adsorption the diffusion models of Boyd and Weber-Morris can be used. The Boyd equation, proposed in 1947, suggested that the film diffusion is the rate limiting step. The equation can be written as follows:

$$\ln\left(1 - \frac{a}{a_e}\right) = -k_{p1} t, \quad (5)$$

where  $k_{p1}$  ( $\text{min}^{-1}$ ) is liquid film diffusion constant [21]. Weber-Morris model assumed that the intraparticle diffusion is the sole rate-limiting step. In this case, the amount of adsorbed substance was linked with adsorption time by the following equation:

$$a = k_{\text{int}} \cdot t^{1/2}, \quad (6)$$

where  $k_{\text{int}}$  is the intraparticle diffusion rate constant. Additionally, a Dumwald-Wagner model was used:

$$\log\left(1 - \left(\frac{a}{a_e}\right)^2\right) = -\frac{K}{2.303} t, \quad (7)$$

where  $K$  ( $\text{min}^{-1}$ ) is the rate constant of adsorption.

## Results and discussion

On Figure 1 the kinetic curves of the adsorption of D-menthol and L-menthol on silica gel modified with o-toluic acid crystals,

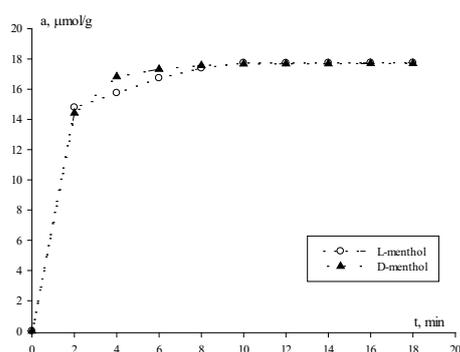


Fig. 1. Adsorption curves of menthols on o-toluic acid crystals obtained under Viedma ripening conditions.

obtained under Viedma ripening conditions, were shown. As can be seen from the presented data, the kinetic curves of enantiomers adsorption have differed. Before reaching equilibrium, D-menthol was adsorbed more strongly than L-menthol. Thus, after 2 minutes, the L-menthol adsorption was 14.8  $\mu\text{mol/g}$ , while the adsorption of D-menthol was 15.7  $\mu\text{mol/g}$ . The enantioselectivity coefficient  $\alpha$ , calculated as the ratio of higher adsorption to lower adsorption, was 1.06. After 4 minutes, the largest difference in adsorption values was observed. They were 15.8 and 16.8  $\mu\text{mol/g}$  for L-menthol and D-menthol, respectively ( $\alpha=1.07$ ). At the 6th minute, the adsorption value of L-menthol was 16.7  $\mu\text{mol/g}$ , D-menthol – 17.3  $\mu\text{g/ml}$  ( $\alpha=1.04$ ). By 8 minutes, adsorption-desorption equilibrium was reached, and no differences in adsorption values were observed. Thus, the analysis of the obtained kinetic curves made it possible to assume differences in the adsorption rate.

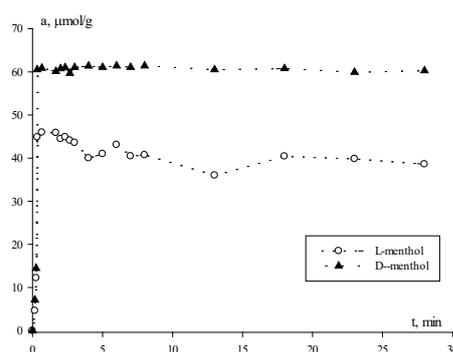


Fig. 2. Adsorption curves of menthols on  $\text{CsCuCl}_3$  crystals obtained under Viedma ripening conditions.

Figure 2 has shown the kinetic curves of adsorption on silica gel modified with  $\text{CsCuCl}_3$  crystals. As can be seen from the obtained data, the adsorption curves of menthol enantiomers have also differed. It should be noted that the time of establishment of adsorption equilibrium between the modified samples has differed too. Thus, in the case of  $\text{CsCuCl}_3$ , adsorption equilibrium was established already at 20 s, which is 24 times faster than in the sample with o-toluic acid.

The t-test was used to prove the relevance of the difference in the adsorption values of enantiomers. This statistical method consists in proposing and testing a null hypothesis about the coincidence of two sets of parallel data by comparing the experimental values of the t-test and the extreme boundary value tabulated depending on the number of measurements and the confidence level. If the experimental value is below the extreme value ( $\alpha=0.05$ ), this indicates that the two values

Table 1. Values of t-criterion and F-criterion for pairs of values of menthol adsorption on crystals of o-toluylic acid and  $\text{CsCuCl}_3$  (critical degree of significance  $\alpha=0.05$ )

o-toluylic acid		
t, min	t-test	F-test
2	0.0017	fulfilled
4	$9.95 \cdot 10^{-7}$	fulfilled
6	$2.87 \cdot 10^{-7}$	fulfilled
8	$1.30 \cdot 10^{-3}$	fulfilled
$\text{CsCuCl}_3$		
t, s	t-test	F-test
10	0.0147	fulfilled
15	0.0230	fulfilled



are different. In this work, the null hypothesis was the assumption that the adsorption values of menthol enantiomers belong to the same sample set. Using the t-test, the adsorption values of menthol enantiomers on enantiomorphic crystals of o-toluic acid and  $\text{CsCuCl}_3$  were processed until equilibrium was reached. Previously, the dispersions of all experimental data were checked for homogeneity using the F-test. In all cases, the dispersions were homogeneous. The obtained data of the  $p$  values of the t-test are given in Table 1. As can be seen from the obtained values, the difference in adsorption values is statistically significant for the sample modified with both o-toluic acid and  $\text{CsCuCl}_3$ . Thus, the fact of the difference between the kinetic curves of menthol enantiomers adsorption on the studied adsorbent samples was confirmed.

In the case of menthols adsorption on silica gel modified with  $\text{CsCuCl}_3$ , due to the high rate of establishment of adsorption-desorption equilibrium, the use of various kinetic models was difficult. Therefore, the experimental curves were approximated only for the adsorption of menthols on silica gel modified with o-toluic acid.

In Figure 3, the kinetics of menthols adsorption in the coordinates of Lagergren's pseudo-first-order model was described. It can be seen from the figure, that the adsorption kinetics was adequately described only for D-menthol. This was confirmed by high correlation coefficients (Table 3). Hence, in the case of D-menthol, the limiting stage was the diffusion to the adsorbent, and in the case of L-menthol, it can be otherwise. By Lagergren's model, the rate constants of adsorption were calculated (Table 3). For L-menthol the rate constant was  $0.7766 \text{ min}^{-1}$ , while for D-menthol it was  $0.4781 \text{ min}^{-1}$ .

Ho and McKay's pseudo-second order equation is widely used to describe the kinetic laws of adsorption. The plotting of curves (Fig. 4) in the  $t/a - t$  coordinates makes it possible to analyze the experimental data from the point of view of the Ho and McKay rate model. As can be seen from

the graph, this model was able to adequately describe the experimental data on the adsorption kinetics for both D- and L-menthol. The results of the determination made it possible to calculate the reaction rate constants equal to  $0.08 \text{ g}/(\mu\text{mol}\cdot\text{min})$  and  $0.17 \text{ g}/(\mu\text{mol}\cdot\text{min})$  for L-Menthol and D-Menthol, respectively.

The Elovich model, simplified by Chen and Clayton [15], was used to estimate the adsorption and desorption constants. Data linearization in the coordinates of the Elovich model also did not cause difficulties (Fig. 5). The equation constants can be determined by drawing the dependence  $a - \lg t$  from the slope and the segment cut off by the straight line on the y-axis. The initial rate constant ( $\alpha$ ) of adsorption and desorption constant ( $\beta$ ) for L-menthol were  $820 \mu\text{mol}/\text{g}\cdot\text{min}$  and  $0.51 \mu\text{mol}$  respectively, while for D-menthol  $\alpha$  and  $\beta$  were  $386000 \mu\text{mol}/\text{g}\cdot\text{min}$  and  $0.85 \mu\text{mol}/\text{g}$ , respectively. From the data obtained, it is noticeable that the adsorption equilibrium in the case of both samples is shifted to the right. The dependence in the values of the adsorption rate constants has coincided with the previous methods - D-menthol was adsorbed faster than L-. Differences were observed only in the ratio of rate constants.

The Lagergren, Ho and McKay and Elovich models were used only for comparing adsorption rate constants of enantiomers. From the data obtained one can see the different kinetics of adsorption for enantiomers. Enantiomer diffusion in solution should be equal because of solvent achiral nature. So, if diffusion was rate-limiting step, no enantioselectivity should be observed. One can conclude that the rate-limiting step was adsorption.

From this insight, it is interesting to analyze the results of curve approximation using the diffusion models. Thus, Boyd model describes diffusion out of particle, but it has approximated the experimental data with high

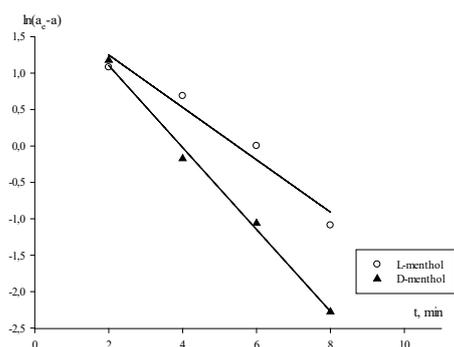


Fig. 3. Description of the kinetics of adsorption of menthols in the coordinates of Lagergren's pseudo-first-order model.

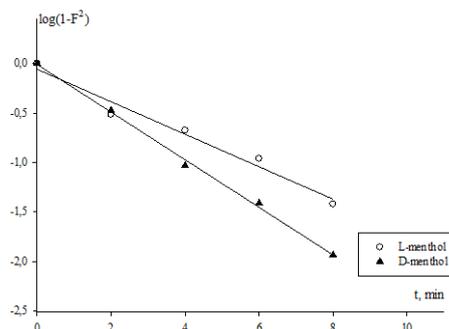


Fig. 4. Description of the adsorption kinetics of menthols in the coordinates of the Dumwald-Wagner model

Table 2. Parameters of approximation of the o-toluic acid kinetic curve by the models used

Model name	Parameter	L-Menthol	D-Menthol
Pseudo-first order of Lagergren	Rate constant	0.36	0.56
	R	0.977	0.997
Pseudo-second order Ho and McKay	Adsorption rate constant	0.080	0.11
	R	0.999	0.999
The Elovich model	The constant of the initial rate of adsorption	1152	2435
	Desorption constant	0.51	0.57
	R	0.983	0.927
Weber-Morris model	Intraparticle diffusion rate constant.	6.18	6.38
	R	0.936	0.941
Boyd Model	Kinetic coefficient	0.45	0.63
	R	0.973	0.994
The Dumwald-Wagner model	Rate constant of adsorption	0.38	0.55
	R	0.986	0.999

correlation coefficients. Moreover, the kinetic coefficients for enantiomers have differed. The Weber-Morris model wasn't fit data well, unlike of Dumwald-Wagner equation (see Fig. 4). The last has shown the best fitting among the diffusion models used. Non-linearity  $a - t^{1/2}$  dependences in the coordinates of the Weber-Morris equation could indicate a potential mixed-diffusion mechanism of adsorption kinetics, when the process cannot uniquely limited by external or internal diffusion.

So, there can be two points of view on kinetic mechanism. From the one hand, the results of approximation can indicate the mixed mechanism, with diffusion and adsorption rate are closed to each other. In the other hand, the absence of dependence between the fitting results of pseudo-first- and pseudo-first-order rate equations and kinetic mechanisms was thoroughly proved by Khamizov [22-24]. So there is a question, how we can trust to use the fitting quality to making conclusions about kinetic mechanism. Maybe a good fitting of experimental

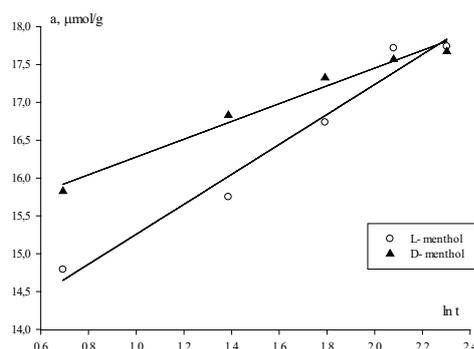


Fig. 5. Description of the adsorption kinetics of menthols in the coordinates of the Elovich models

data by Boyd model has only a mathematical nature.

### Conclusion

Thus, the reliable differences in enantiomers adsorption values in the region before adsorption–desorption equilibrium were reached. The difference in adsorption rate constants was observed as well. It has indicated that the adsorption rate of menthol enantiomers on crystals of *o*-toluic acid and  $\text{CsCuCl}_3$  obtained under Viedma ripening conditions was different. This phenomenon

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was discovered for the first time in this work. Differences in the kinetics of adsorption of enantiomers on adsorbents with a supramolecular chiral surface open up new opportunities for developing technologies for the separation of optical isomers.

### Конфликт интересов

Авторы заявляют, что у них нет известных финансовых конфликтов интересов или личных отношений, которые могли бы повлиять на работу, представленную в этой статье.

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