



УДК 543.867:661.183

## Equilibrium of the acid-activated system clinoptilolite tuff – ethanol solution of $\beta$ -carotene

Kotova D.L.<sup>1</sup>, Vasilyeva S.Yu.<sup>1</sup>, Krysanova T.A.<sup>1</sup>,  
Borodina E.V.<sup>2</sup>, Davydova E.G.<sup>3</sup>

<sup>1</sup>*Voronezh State University, Voronezh*

<sup>2</sup>*Debye Institute for Nanomaterials Science, Department of Inorganic Chemistry and Catalysis, Utrecht*

<sup>3</sup>*Voronezh State University of Architecture and Civil Engineering, Voronezh*

Received 18.03.2014 г.

### Аннотация

The equilibrium of the acid- activated system of clinoptilolite tuff - solution of ethanol of  $\beta$  - carotene was studied in this work. The change in the mechanism of interaction of the system with increasing concentration of provitamin A was evaluated based on the analysis of the isotherm. The adsorption of  $\beta$ -carotene from dilute solutions was described by Langmuir model. Monolayer fixing of sorbate within the structural matrix of the sorbent was determined by the formation of hydrogen bonds between provitamin A and isolated silanol groups. Formation of polymolecular layers due to the association of  $\beta$ -carotene provided by hydrophobic interactions. Nitrogen physisorption was utilized to observe changes in the surface area properties, porosity of the zeolite after the adsorption of  $\beta$ -carotene.

**Keywords:**  $\beta$  – carotene, clinoptilolite tuff, adsorption, isotherm

В работе проведено исследование равновесия в системе кислотно-активированный клиноптилолитовый туф – этанольный раствор  $\beta$  – каротина. На основе анализа изотермы установлено изменение механизма взаимодействия в системе с ростом концентрации провитамина А. Адсорбция бета-каротина из разбавленных растворов описана моделью Ленгмюра. Монослойное закрепление сорбата в структурной матрице сорбента определяется образованием водородных связей между провитамином А и изолированными силанольными группами. Формирование полимолекулярных слоев в результате ассоциации бета-каротина осуществляется за счет гидрофобных взаимодействий. Методом низкотемпературной адсорбции / десорбции азота рассмотрено изменение поверхностных свойств, пористости сорбента после закрепления  $\beta$  – каротина.

**Ключевые слова:**  $\beta$  – каротин, клиноптилолитовый туф, сорбция, изотерма

### Introduction

Selective adsorption of vitamins and pharmaceuticals on natural sorbents may be used for the analytical determination of the component, as well as for extraction and concentration of the desired products from the complex mixtures [1-5]. The possibility of using aluminosilicates, as carriers for biologically active compounds has been reported in the literature [2-4]. One of the most valuable representatives of aluminosilicates is clinoptilolite having micro - mesoporous structure, high adsorption, ion-exchange and molecular sieve properties [2, 6, 7]. Acidizing of clinoptilolite allows changing of the textual characteristics and the hydrophilic - hydrophobic balance matrix of the sorbent.

The most important biologically active drug is  $\beta$ -carotene (a precursor of vitamin A) involved in antioxidant protection [8, 9]. In [3, 4, 10] the results of studies on the mechanism of fixing of  $\beta$ -carotene on various natural and synthetic sorbents. The authors of [3] studied the adsorption of  $\beta$ -carotene on native and acid-activated bentonite. It is shown that the amount of adsorbed provitamin A increases by 5.5 times after treatment of bentonite 2.0 M  $\text{H}_2\text{SO}_4$ . There is evidence [10] about the impact on textural characteristics of the sorbent, temperature and the nature of the solvent used on the amount of adsorption of  $\beta$ -carotene. This paper presents the results of studying patterns of sorption  $\beta$ -carotene (provitamin A) from ethanol solution of the acid-activated clinoptilolite tuff recommended for use as enterosorbent.

## Experimental

In our work we used provitamin A ( $\beta$ -carotene) produced by Sigma(Germany). Structural formula of  $\beta$ -carotene is presented in Fig. 1.

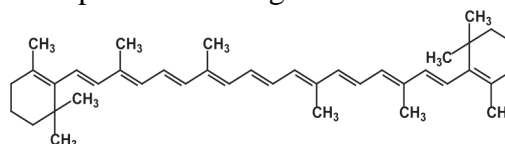


Fig. 1. Structural formula of provitamin A

Adsorption of  $\beta$ -carotene was investigated for zeolite tuff (used as a sorbent) of Lulinskoe deposit at Yugra, near-polar Ural. The tuff represented a multi-phase mixture where the main phase was clinoptilolite (68%). Impurity phases of quartz, calcite (15%), phillipsite (6%), minerals of montmorillonite family (8%) were found as well some other impurities [7]. According to the experimental data, as a result the acidizing sorbent 4.0M hydrochloric acid occurs dealumination (molar Si/Al ratio increases from 3.9 to 10.5), the exchange of extra framework aluminate cation fragments in the remaining matrix on hydrogen ion and the formation associated and isolated of silanol groups, while maintaining its crystalline structure. By acid activation of clinoptilolite accessible pore for penetration of large organic molecules. It also increase selectivity for apolar compounds by changing the hydrophilic- hydrophobic balance of the sorbent.

Acid activation of clinoptilolite tuff was carried out by treating it with a 4.0 M hydrochloric acid solution at  $295 \pm 2$  K. After sample humidity had been determined, a 0.02 to 0.06 mm fraction of air-dried zeolite tuff ( $1.0 \pm 0.0002$  g) was brought into contact with an HCl solution ( $100.0 \text{ cm}^3$ ) and the mixture was stirred for 4 h at a preset temperature [7]. The equilibration time was determined in a preliminary experiment. The sorbent was filtered off from the solution and washed with distilled water until no chloride ions were detected in the filtrate.

Sorption equilibrium in the system of “acid-activated clinoptilolite tuff (fraction of 0.02-0.06 mm) – ethanol solution of  $\beta$ -carotene” was studied at the temperatures of  $295 \pm 2$  K under static conditions by variable concentrations technique. The range of the used concentrations of  $\beta$ -carotene was of  $1.40 \cdot 10^{-2} - 30.0 \text{ mmol/dm}^3$ . The sample of clinoptilolite tuff of 0.050 ( $\pm 0.0002$ ) g in mass in the air-dry state was put in contact with  $200.0 \text{ cm}^3$  of the investigated  $\beta$ -carotene solution with the known concentration and stored at the given temperature under continuous agitation for 2.5 hours. Equilibrium phases were separated and analyzed for  $\beta$ -carotene content by spectrophotometric method with the use of spectrometer BioSpec-mini produced by Shimadzu for  $\lambda = 452 \text{ nm}$  ( $S_r = 0.05$ ). Control

for the amount of the adsorbed  $\alpha$ -tocopherol was performed by the difference of the concentrations in solution before and after contact with the sorbent.

IR-spectra of the samples were measured with the use of spectrometer Bruker Equinox 55 with Fourier-transform operating in the diffuse reflection (DRIFT) mode within the frequency range of 400-4000  $\text{cm}^{-1}$ . Interpretation of spectra was performed using the literature data [4,8,12-15].

Method sorption / desorption of nitrogen was used to determine changes in textural characteristics clinoptilolite tuff after sorption provitamin A. Adsorption / desorption of nitrogen was made with the device Quadrasorb-SI MP (Quantachrome, USA) at 77 K and the relative pressure of  $10^{-5}$ -0.99. The samples were preliminarily degassed at the temperature of 392 K in vacuum for eight hours. Basing on the measured isotherms the surface area, volume, diameter and pores size distribution were determined. Brunnauer-Emmet-Teller (BET) equation was used for the calculation of the samples surface area [16]. Barreth-Joyner-Halend (BJH) method [17] was applied for the determination of the pores size distribution. Volume of micropores ( $V_{\text{micro}}$ ) was calculated using t-segment technique [18].

## Results and discussion

It has been established that  $\beta$ -carotene is non-adsorbable on native clinoptilolite tuff. Interfacial distribution of vitamin A in the sorption process is shown in Fig. 2. Isotherm of Sorption  $\beta$ -carotene on acid-activated clinoptilolite tuff relates to IV type IUPAC and Giles classification corresponds to S-form, indicating that the nature of the polylayer adsorption. The maximum sorption capacity of 3.50 mmol/g.

At the initial segment an isotherm is characterized by the linear dependence of the attached  $\beta$ -carotene on the sorbent on the concentration of solution, and after that it is transformed into a plateau, meaning monolayer adsorption.

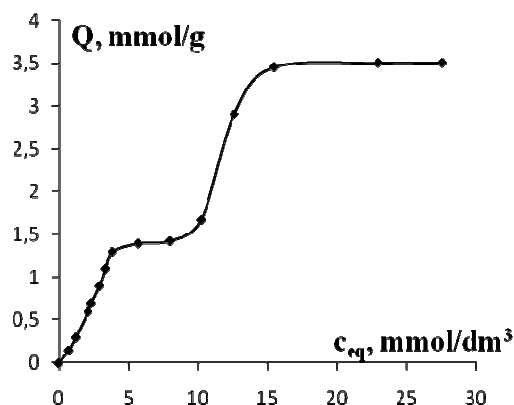


Fig. 2. Isotherms of  $\beta$ -carotene adsorption on acid-activated clinoptilolite tuff

To describe the initial portion of an isotherm was used Langmuir equation [19]:

$$Q = \frac{Q_{\infty} K c_p}{(1 + K c_p)} \quad (1)$$

where  $K$  – adsorption equilibrium coefficient,  $\text{dm}^3/\text{mmol}$ ;  $Q$  is amount of the adsorbed  $\beta$ -carotene, mmol/g;  $Q_{\infty}$  – is the limiting amount of adsorbed  $\beta$ -carotene (monolayer capacity), mmol/g;  $c_{\text{eq}}$  – is equilibrium solution concentration,  $\text{mmol}/\text{dm}^3$ .

Representation the experimental data to a linear form in the coordinates

$$\frac{1}{Q} = \frac{1}{Q_{\infty} K c_p} + \frac{1}{Q_{\infty}} \quad (2)$$

allowed to graphically determine the limit of the monolayer capacity and the coefficient of sorption equilibrium, which amounted to 1.42 mmol / g and 0.540 dm<sup>3</sup> / mmol.

To confirm compliance obtained sorption isotherm equation Langmuir sorption equilibrium and calculation of the coefficient dependence  $C_{eq} / Q$  from  $c$  in the range of equilibrium concentrations of  $\beta$  - carotene  $1.3 \cdot 10^{-2} - 27.5$  mmol/dm<sup>3</sup> treated MNCs, according to the linear form of equation (2). The resulting value of the correlation coefficient (0.99) indicates a satisfactory conformity of the Langmuir isotherm equation in the range of concentrations.

In the IR spectrum of the acid-activated clinoptilolite tuff are present distinct absorption bands at 3754 and 3253 cm<sup>-1</sup>, respectively, corresponding to the isolated and associated silanol groups [12,13]. Maximum absorption at 930 cm<sup>-1</sup> characterizes the vibration of Si-O to Si-OH groups linked together by hydrogen bonds. Fixing  $\beta$ -carotene in the matrix of sorbent is reflected in the appearance of the absorption bands of the spectrum at 1420 cm<sup>-1</sup> and within the range of 3000-2800 cm<sup>-1</sup> (2850, 2920, 2980), characterizing valence and deformation vibrations of C-CH<sub>3</sub> and C-CH<sub>2</sub> – sorbate groups. Vibrations of C=C bound in the aromatic ring were revealed at 1540 cm<sup>-1</sup>.

Active centers on the surface of the acid-activated sorbent presented isolated and coupled silanol groups which can interact with  $\beta$ -carotene. After adsorption of provitamin A one can observe a decrease of intensity of the peak at 3754 cm<sup>-1</sup>, corresponding to the isolated silanol groups. According to published data [3,20], the most reactive bond in  $\beta$ -carotene is the 7-8 double bond, and the main reactive center of the molecule toward and type of attack is the seventh carbon atom. Thus, the localization of  $\beta$ -carotene on the surface of the sorbent can be due to the formation of a hydrogen bond with isolated of silanol groups (Fig. 3)

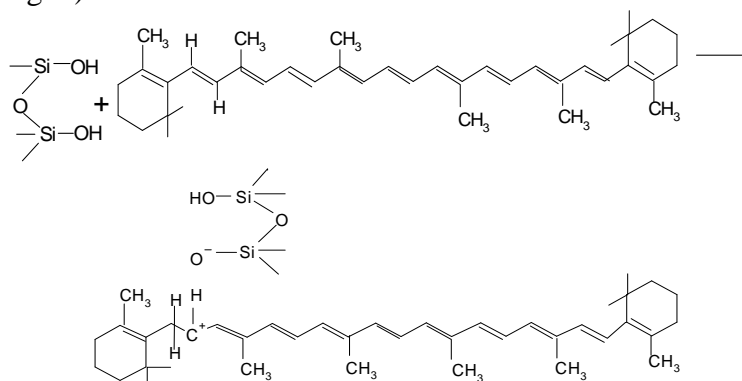


Fig. 3. Scheme of interaction in the system  $\beta$ -carotene - an acid-activated clinoptilolite tuff

The monolayer of fixing  $\beta$ -carotene leads to the shielding of surface, i.e. access to the isolated silanol group is impeded. At concentrations above provitamin 10.0 mmol / dm<sup>3</sup> additional absorption of provitamin A occurs. On the surface of sorbent formed polymolecular of layers  $\beta$ -carotene in the form of associations of vitamin. Formation of structural associates possibly as a result of hydrophobic interactions between the molecules of provitamin A.

Obtained adsorption / desorption isotherms of nitrogen for acid- activated clinoptilolite tuff before and after fixing  $\beta$ -carotene (Fig. 4) . In accordance with IUPAC isotherms are IV type with a wide hysteresis loop not closing at low relative pressures. The

authors of [ 21,22 ] explain this as a limitation of nitrogen diffusion through microporous structural constriction and the presence of wedge-shaped pores. Sorption pro-vitamin A on the surface of acid - activated aluminosilicate reduces the amount adsorbed of nitrogen (Fig. 4). Table 1 shows the structural characteristics of the sorbents, determinate from analysis of isothermal adsorption / desorption of nitrogen. A decrease in the mesopore volume and the specific surface area relative to the initial sample of the sorbent was observed.

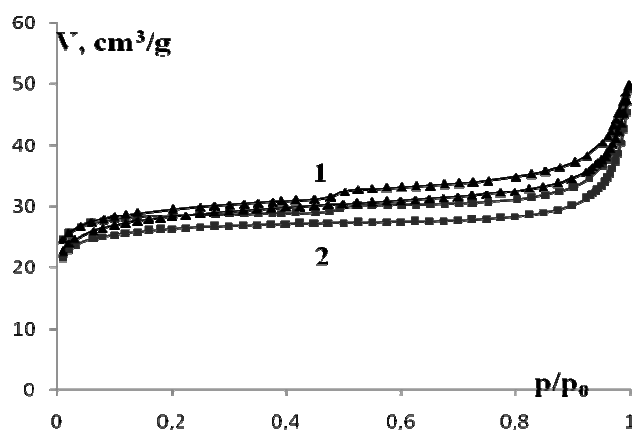


Fig. 4 Isotherms of low-temperature adsorption/desorption of nitrogen for the clinoptilolite tuff: 1- acid-activated, 2 – after sorption of  $\beta$  - carotene

Table. 1. Parameters of the porous structure, calculated using the adsorption / desorption of nitrogen

Clinoptilolite tuff	Surface area, m <sup>2</sup> /g		Volume of pores cm <sup>3</sup> /g		
	$S_{\text{BET}}$	$S_{\text{BJH}}$	$V_{\text{total}}$ (BET)	$V_{\text{meso}}$ (BJH)	$V_{\text{micro}}$ (t-plot)
Before sorption of $\beta$ - carotene	92.3	56.9	0.077	0.049	0.030
After sorption of $\beta$ - carotene	84.8	48.0	0.075	0.042	0.030

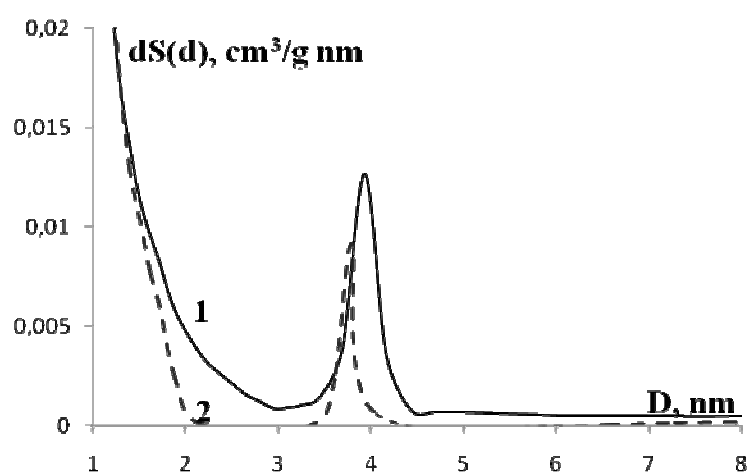


Fig. 5. Curves for pore size distribution in clinoptilolite tuff: 1- acid-activated, 2 – after sorption of  $\beta$ -carotene

Pore size distribution in the mesoporous structure of clinoptilolite tuff defined by the model BJH, presented in Fig. 6. It is obvious that in the course fixing on the surface of

provitamin A sorbent can be expected not only to reduce the amount of adsorbed nitrogen (Fig. 4), but also decreasing the pore size (Fig. 5). For acid-activated clinoptilolite tuff dominated by mesopores of 3.9 nm. Filling of mesopores with  $\beta$ -carotene reduces the amount and size of pores. For aluminosilicate after adsorption of  $\beta$ -carotene the pore diameter is 3.6 nm.

## Conclusion

The regularities of adsorption of  $\beta$ -carotene from an ethanol solution on the acid-activated 4.0 M HCl clinoptilolite tuff was found. It is shown that at low concentrations, the adsorption isotherm is described by the Langmuir equation. It has been shown that the mechanism of the sorption is altered by increasing solute concentration due to the formation of  $\beta$ -carotene associates. Monolayer capacity limit and the coefficient of sorption equilibrium was calculated. It was established that  $\beta$ -carotene sorption leads to changes in texture characteristics. These are manifested in a decrease in specific surface area, pore number and size of the sorbent.

## Acknowledgements

Authors are sincerely grateful to Joseph A. Stewart (Debye Institute for Nanomaterials Science Inorganic Chemistry and Catalysis, Utrecht University, The Netherlands) for their help with translating articles.

## References

1. Farias T., Ruiz-Salvador A.R., Rivera A Interaction studies between drugs and a purified natural clinoptilolite // Micropor. Mesopor. Materials. 2003. V. 61. P. 117-125.
2. Rivera A., Farias T. Clinoptilolite – surfactant composites as drugs support: A new potential application // Micropor. Mesopor. Materials. 2005. V 80. P. 337-346.
3. Gonzalez- Pradas E., Villafranca- Sanchez M., Valverde- Garcia A. Adsorption of  $\beta$  – carotene from acetone solution on natural and chemical modified bentonite // Materials Chemistry and Physics. 1991. V 27. P. 307-319.
4. Sarier N, Guler C.  $\beta$ -carotene adsorption on acid-activated montmorillonite // JAOCs. 1988. V.65. P 776-779.
5. Ahmad A.L., Chan C.Y., Mashitan M.D. Adsorption kinetics and thermodynamics of  $\beta$ -carotene on silica – based adsorbent // Chem. Engene. J. 2009. V. 148. № 2-3. P. 378-384.
6. Kotova D.L., Vasilyeva S.Y., Krysanova T.A. et al. Isotherm of  $\alpha$ -Tocopherol Adsorption on Acid Activated Clinoptilolite Tuff // Colloid Journal. 2013. V. 75. № 1. P. 84-87.
7. Kotova D.L., Do Thi Long, Krysanova T.A. et al. Kislotnay aktivaciy clinoptilolitovogo tufa mestorochdeniy Pripolynogo Urala Ugru // Izv.Vyshh. Uchebn. Zaved., Khim. Khim. Tekhnol. 2012, V. 55. №. 4. P. 100-104. [in Russian]
8. Dychevko A.A. Vitamin A: Obmen u fynksii. Kiev. Nayka, 1989. 288 p. [in Russian]
9. Savinov B.G. Carotene (provitamin A) u poluchenie ego preparatov. Kiev. Nayka 1948. 231 p.

10. Muhammad, Khan M. A., Choong T. S. Y. et al. Kinetics studies for the adsorption of  $\beta$ -carotene on mesoporous carbon coated monolith: effect of concentration and temperature // *Asian Journal of Chemistry*. 2012. V. 24. No. 7. P. 3155-3161
11. Kotova D.L., Vasilyeva, S.Yu., Krysanova T.A. Adsorbtsia  $\alpha$ -tocopherola is etanolnogo rastvora na kislotno-aktivirovannom clinoptilolitovom tufe // *Sorbts. Khromatogr. Protsessy*. 2012. V. 12. № 6. P. 901–908. [in Russian].
12. Garcia-Basabe Y., Rodriguez-Iznaga I., de Menorval L.C. et al. Step-wise dealumination of natural clinoptilolite: Structural and physicochemical characterization // *Microporous and Mesoporous Materials*. 2010. V. 135. P.187-196.
13. Beyer H.K. Dealumination Techniques for Zeolites // *Molecular Sieves - Science and Technology*. 2002. V. 3. P. 203-255.
14. Nakanisi K. Infrared spectroscopy and the structure of organic compounds. M.: Mir. 1987. [in Russian].
15. Kasicina L.A., Kypetskay N.B. Primenenie UF-, IK- and YMR-spektroskopii v organ. himii. M.: Vyssh. shkola, 1971. 264 p. [in Russian].
16. Brunauer S., Emmett P., Teller E Adsorption of Gases in Multimolecular Layers // *J. Amer. Chem. Soc.* 1938.V.60. P. 309.
17. Barrett E.P., Joyner L.G., Halenda P.P.J. The Determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms // *J. Am. Chem. Soc.* 1951. V. 73. P. 373.
18. Sprynskyy M., Golembiewski R., Trykowski G. Heterogeneity and hierarchy of clinoptilolite porosity // *J. of Physics and chemistry of solids*. 2010. V. 71. P. 1269.
19. Gregg S.J., Sing K.S.W. Adsorption, Surface Area and Porosity, Academic Press, 1982. 304 p.
20. Nihal Sarier, Guler C. The mechanism of beta-carotene adsorption on activated montmorillonite // *JAOCS*. V. 66. №. 7. 1989. P. 917-923.
21. Zhao X.S., Lu G.Q., Whittaker A.K. et al. Modification of MCM-41 by Surface Silylation with Trimethylchlorosilane and Adsorption Study // *J. Phys. Chem. B*. 1998. 102. P. 1556.
22. Yang H., Zhang G., Hong X. et al Silytion of mesoporous silica MCM-41 with the mixture of  $\text{Cl}(\text{CH}_2)_3\text{SiCl}_3$  and  $\text{CH}_3\text{SiCl}_3$ : combination of adjustable grafting density and improved hydrothermal stability // *Microporous and mesoporous materials*. 2004. 68. P. 119.

---

**Kotova Diana L.** - Doctor of Science, professor of analytical chemistry department of chemical faculty, Voronezh State University, Voronezh

**Vasilyeva Svetlana Yu.** - the post-graduate student of analytical chemistry department of chemical faculty, Voronezh State University, Voronezh

**Davydova Ekaterina G.** - head of department of innovative and investment programs and projects, Voronezh State University of Architecture and Civil Engineering, Voronezh

**Krysanova Tatyana A.** - lecturer of analytical chemistry department of chemical faculty, Voronezh State University, Voronezh

**Borodina Elena V.** – postdoctoral fellows Debye Institute for Nanomaterials Science, Department of Inorganic Chemistry and Catalysis, Utrecht