Adsorption of water by clinoptilolite and glauconite

Kotova D.L.[1], Artamonova M.N.[1], Krysanova T.A.[1],
Novikova L.A.[2], Belchinskaya L.I.[2]

[1]FSBEI HE "Voronezh State University", Voronezh
[2]FSBEI HE "Voronezh State University of Forestry and Technologies named after G.F. Morozov", Voronezh

Adsorption of water molecules by clinoptilolite and glauconite was studies by isopiestic method within a wide range of water activity. A quantitative assessment of hydration properties of sorbents was given. The regularities of water adsorption caused by the structural features of the sorbents were determined and explained. The adsorption theory of Brunauer, Emmett and Teller (BET) was applied for description of water adsorption by aluminosilicates. It was shown that the first monomolecular layer of the adsrobate is formed due to interaction of water molecules with extra framework cations and electronegative sites of sorbent framework.

Keywords: adsorption, isopiestic method, clinoptilolite, glauconite.

Адсорбция воды клиноптилолитом и глауконитом

Котова Д.Л.[1], Артамонова М.Н.[1], Крысанова Т.А.[1],
Новикова Л.А.[2], Бельчинская Л.И.[2]

[1]ФГБОУ ВО «Воронежский государственный университет, Воронеж
[2]Воронежский государственный лесотехнический университет им. Г.Ф. Морозова, Воронеж

Методом изопиестирования изучена адсорбция молекул воды клиноптилолитом и глауконитом в широком интервале активности воды. Дана количественная оценка гидратационным свойствам сорбентов. Установлены и объяснены закономерности адсорбции воды, обусловленные структурными особенностями сорбентов. Адсорбция воды алюмосиликатами описана с применением адсорбционной теории БЭТ. Показано, что образование мономолекулярного слоя адсорбата протекает в результате взаимодействия молекул воды с внекаркасными катионами и электроотрицательными центрами матрицы сорбентов.

Ключевые слова: адсорбция, изопиестирование, клиноптилолит, глауконит

Introduction

Natural inorganic sorbents are different in their composition, structural characteristics, physical-chemical and adsorption properties that allow their application in various fields of industry. Aluminosilicates are a phase-separating system, in which a solvent, water, distributes between the moveable extra framework cations, the negatively charged lattice of the sorbent and the fragments of structural cavities. The chemical composition and the structure of aluminosilicates directly influence their adsorption, ion-exchange and molecular sieving characteristics, while the amount and the state of water in their structure determine the equilibrium and transport characteristics of sorption.

Currently, there are several points of view regarding the nature and the state of the water in zeolites [1-4]. As being referred to, the one of the factors affecting the sorption selectivity of components is the hydration ability of the sorbent, which is determined by the pore structure, chemical nature of the surface and the extra framework cations.

It is of an interest to experimentally study and to consider the influence of the aluminosilicates structures, namely, those from natural clinoptilolite and glauconite, on the features of their interaction with water in the wide activity range, as well as to give a quantitative assessment of the hydration characteristics of the sorbents.

Experimental

The natural zeolite sample (Clin) originating from Slovakia, was a mixture of 95% of clinoptilolite and 5% of illite [5]. It is a characteristic feature of clinoptilolite to have a regular tetrahedral structure, in the gaps of which hydrated cations and water molecules are allocated. The negative charge of the framework $(AlO_4)^-$ and the compensating it positive charge of the extra framework cations determine the local distribution of the charge on the surface of cavities and channels available for water molecules [6, 7]. The major extra framework cations of the investigated clinoptilolite were, mainly, K^+ and Ca^{2+}, as well as Mg^{2+} and Na^+ (Table 1), the concentration of which was 117 mmol/100 g [8] according to its cation-exchange capacity (CEC) value. The molar ratio of Si/Al, determining the hydrophilic-hydrophobic properties of clinoptilolite, was 5.5. The total pore volume was 0.44 cm^3/g, the average pore diameter was about 11.05 nm [5, 9].

Another investigated aluminosilicates was a clay mineral glauconite (Glt) originating from the area of the south-west of the Voronezh anticline, for which its layered structure is a distinguishing feature from that of clinoptilolite [10]. The phase composition of the investigated glauconite samples was represented by the mixed layered minerals (MLM) of the illite-smectite (I-S) series with the layers ratio of 20:80 and 50:50 (swelling component). The elemental analysis of Glt-sample illustrated the presence of water molecules and the exchangeable cations of K^+, Mg^{2+} and Ca^{2+} in the interlayer space [9], the number of which usually lie within 5-10 mmol/100 g [11]. The total pore volume was 0.31 cm^3/g, the average pore diameter was about 5.7 nm [12,13].

Table 1. Elemental compositions of natural clinoptilolite and glauconite

Sample	Element, atom. %											Total
	Na	Mg	Al	Si	K	Ca	Cr	Fe	Ti	Cu	S	
Clin [5]	0.42	0.52	5.50	27.03	2.61	1.76	-	1.02	-	0.87	-	100
Glt [13]	-	1.54	3.66	15.86	1.74	0.42	0.05	4.48	0.11	-	0.05	100

The isopiestic method was used to investigate adsorption of water vapors on the surface of the investigated sorbents within the wide relative pressures of the water vapor (activity of water, a_w) from 0.110 till 0.980 at 295 ± 2 K. Prior the experiments to eliminate the water from the surface, the samples were allowed to reach a constant mass during their thermal treatment at 473 K (Clin) and 423 K (Glt) and subsequently placed above the P_2O_5 for complete dehydration. The dehydrated samples were allowed to reach an isopiestic equilibrium with saturated salt solutions of known water activity. The time necessary to reach the isopiestic equilibrium in the *sorbent-water* system depended on the sorbent nature and the activity of water and came to 3 till 12 days. The amount of absorb water (mmole/g or mg/g of sorbent) at equilibrium state was determined by the gravimetric method ($S_r = 4.86 \cdot 10^{-3}$).

The FTIR-spectroscopy was applied to characterize the change of sorbent composition while hydration. The FTIR-spectra of clinoptilolite and glauconite was registered by the Vertex 70 spectrometer with Fourier transformation in a diffuse reflectance mode (Bruker, Germany) within the 400-4000 cm^{-1} wave number range and a 4 cm^{-1} resolution. The method error was 3%. The attribution of the experimental IR-spectra was done according to the literature [14-16].

Results and discussion

The experimental isotherms of water molecules adsorption by investigated sorbents, which represent a dependence of an amount of adsorbed water (n_w, mmol/g) on its activity (a_w), took the S-shaped form and consisted of three sections (Fig. 1). Each section of the isotherms corresponded to a certain extent of hydration, which is characteristic for a given interval of a_w.
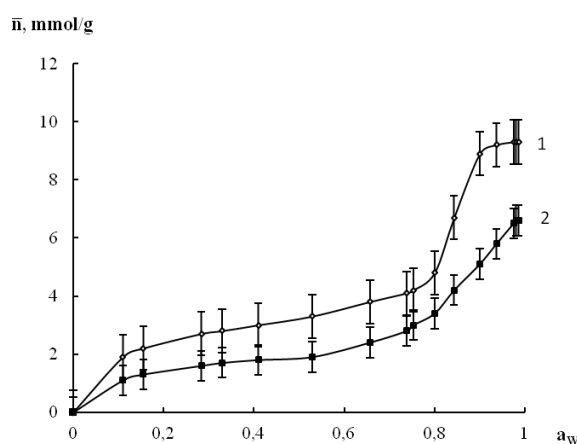

Fig. 1. Isotherms of water adsorption on clinoptilolite (1) and glauconite (2)
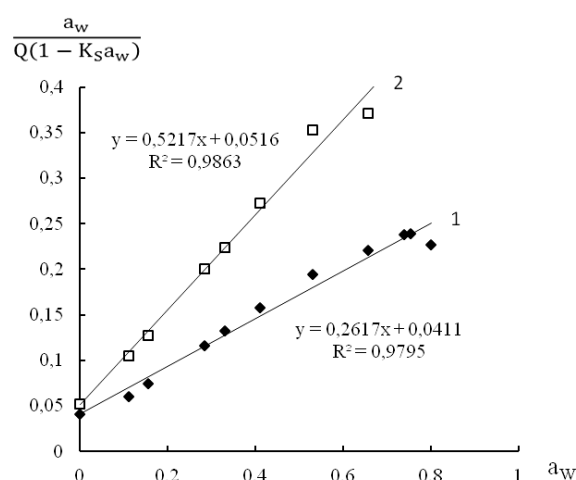
Fig. 2. Linear view of the isotherms of water adsorption by clinoptilolite (1) and glauconite (2) according to linear form of the BET-equation

Hydration of the aluminosilicates in the low water activity range was caused by the ion-dipole interaction of the water molecules with the extra framework cations as well as the electronegative sites of the sorbent lattice [17-19]. Within the a_w range from 0.200 till 0.600 of the isotherm, the amount of water adsorbed was insignificant. One may assume that there was a monomolecular layer of the adsorbate formed. A further sharp increase in the amount of adsorbed water, observed at $a_w > 0.700$, was more expressed for clinoptilolite and related to the filling of the pore space.

As experimental data illustrated, the difference in the hydration properties of the investigated sorbents developed in the whole activity range of water can be caused by the differences in the accessibility and the nature/concentration of the exchangeable cations [2, 20]. The polar water molecules, while permeating the sorbent pores, interact with cations, compensating excessive negative lattice charge of the sorbent. According to the literature, the cation-exchange capacity of the clinoptilolite from Slovakia (117 mmol/100 g [8]) is more than 10-20 times that of natural glauconite samples (5-10 mmol/g [11]). Additionally, the significantly more developed porosity and the surface of zeolites should be taken into account in comparison to weakly swelling layered minerals of illite type (the main structural component of glauconite). As a consequence, the higher hydration characteristics

for zeolite one has to expect. Indeed, the ratio n_{Clin}/n_{Glt} of the amount of water adsorbed respectively by the clinoptilolite and the glauconite samples within the range of a_w from 0.110 to 0.600 was equal 1.7, which, obviously, resulted from the higher concentration of the exchangeable cations in clinoptilolite from one hand, and from their better accessibility, from another hand. At higher water activity range, the adsorption of water by glauconite was 1.4 times lower as compared to clinoptilolite.

Based on the obtained results, one may conclude that at the same amount of the water in the structure of the investigated sorbents, the activity of water was significantly different. Namely, by adsorption of 2 mmol/g of water by the sorbent, the activity of water vapor was about 0.110 for clinoptilolite and 0.529 for glauconite.

To describe the experimental isotherms, the equation of the polymolecular adsorption of BET (1) in a linear view (2) was applied [21, 22]:

$$n = \frac{n_{mono} \cdot K_L \cdot a_w}{(1 - K_S \cdot a_w) \cdot (1 - K_L \cdot a_w + K_L \cdot a_w)}, \tag{1}$$

$$\frac{a_w}{n(1 - K_S \cdot a_w)} = (\frac{K_L - K_S}{n_{mono} \cdot K_L}) \cdot a_w + \frac{1}{n_{mono} \cdot K_L}, \tag{2}$$

where n – amount of adsorbed water at certain water activity (mmol/g); n_{mono} – capacity of a monolayer (mmol/g); a_w – equilibrium water activity; K_L – coefficient, characterizing affinity of water molecules towards adsorbent by the monolayer formation, which is chosen based on the maximal coefficient of linear approximation; K_S – coefficient of adsorption equilibrium.

The high value of the correlation coefficient (R^2) (Table 2) allowed applying the BET theory for describing the isotherms till the $a_w(H_2O)=0.650$ (Fig. 2). It was determined that the value of K_S was significantly lower than K_L that supposed a presumable role of a direct interaction between water molecules and the reaction sites of the sorbents.

Table 2 summarizes the obtained adsorption characteristics, heats of adsorption (Q,kJ/mol) and specific surface areas (S_{sp}, m^2/g) calculated according to equations [4]:

$$RT \ln K_L = Q_I - Q_L, \tag{3}$$

$$S_{sp} = n_{mono} \cdot N_A \cdot \omega, \tag{4}$$

where R – universal gas constant (8.314 J/mol·K); T – absolute temperature (K); K_L – constant of adsorbent affinity towards water molecules in the 1st layer; Q_I – heat of water adsorption in the 1st layer (kJ/mol); Q_L – heat of water condensation ($Q_L=135.9$ J/mol); n_{mono} – monolayer capacity (mmol/g); N_A – Avogadro's number ($6.022 \cdot 10^{23}$ mol^{-1}); ω – area of the adsorbate molecule in the monolayer ($\omega(H_2O) = 10.8 \cdot 10^{-20}$ m^2). The values of S_{sp} indicated the differences in the structure of the investigated sorbents and agree to the data represented in [7, 9].

Table 2. Adsorption and structural characteristics of the sorbents calculated by the BET theory equations

Sorbent	K_L	n_{mono}, mmol/g	K_S	Q_I, kJ/mol	S_{sp}, m^2/g	R^2
Clin	6.37	3.82	0.33	4.7	248.4	0.97
Glt	10.11	1.95	0.40	5.9	126.8	0.98

The observed variations in the hydration ability of clinoptilolite and glauconite were confirmed by the results of the FTIR-spectroscopy (Fig. 3). At the IR-spectra of the aluminosilicates, the presence of water molecules of various strength of interactions and different mutual orientation [1, 17, 20, 23] was derived from the several maxima present

within the range of stretching vibrations 3800-3200 cm^{-1} of water. For clinoptilolite, the absorption band at 3730 cm^{-1} corresponded to vibrations of the free OH-groups. The band at 3630 cm^{-1} testified to formation of water associates. Maxima at 3400 and 3315 cm^{-1} were caused by water molecules localized near the energetically unequal active sites of the clinoptilolite structure.
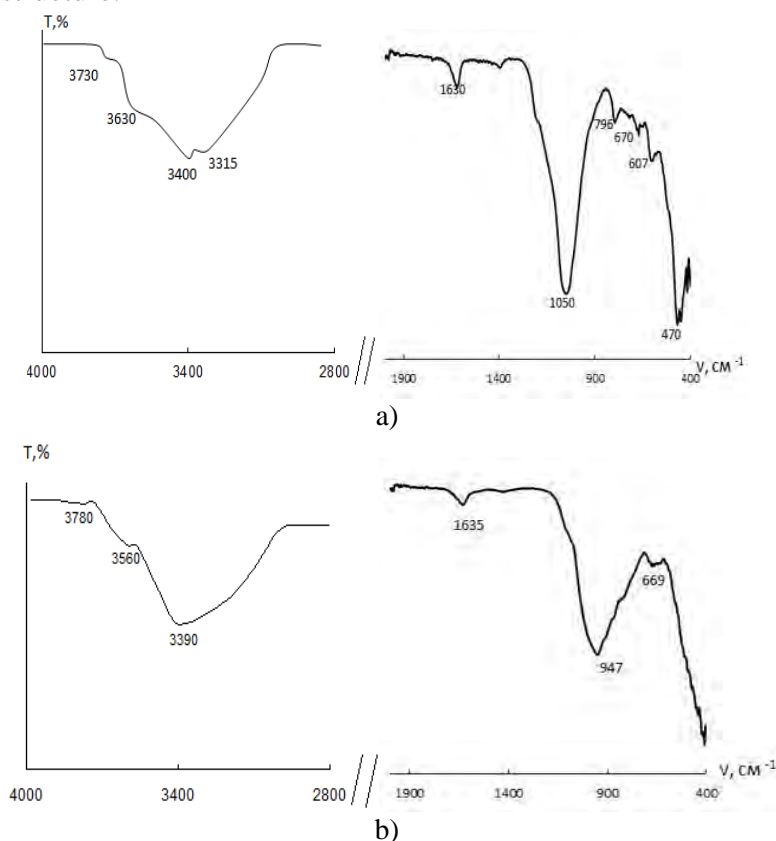

a)

b)
Fig. 3. FTIR-spectra of clinoptilolite (a) and glauconite (b)

For the glauconite sample, the presence of free OH-groups of water was attributed to 3780 cm^{-1} absorption band, whereas the band at 3560 cm^{-1} was typical to OH-groups bound according to "water-water" type. Interaction of water molecules with the active sites of glauconite appeared in the band at 3390 cm^{-1}. Deformation vibrations of water molecules for clinoptilolite and glauconite resulted in absorption bands at 1630 cm^{-1} and 1635 am^{-1}.

Conclusion

The regularities of water molecules adsorption by natural clinoptilolite and glauconite were revealed. The BET theory was applied for describing the adsorption isotherms. The determined quantitative characteristics of hydration of aluminosilicates confirmed were governed by the accessibility of the aluminosilicate structure for the permeation of water molecules as well as by the concentration and the nature of the extra framework cations. The clinoptilolite samples observed higher hydration ability.

References

1. Korkuna O. et al., *Microporous Mesoporous Mater.,* 2006, Vol. 87, pp. 243-254.

2. Alver B.E., Sakizci M., Yorukogullari E., *J. Therm. Anal. Calorim.*, 2010, Vol. 100, pp. 19-26.

3. Arcoya A. et al., *Microporous Mesoporous Mater.*, 1996, Vol. 7, pp. 1-13.

4. Tarasevich Yu.I., Ovcharenko F.D., Adsorption on clay minerals, Kiev: Naukova dumka, 1975, 352 p.

5. Belchinskaya L.I. et al., *Physical chemistry of surface and protection of materials,* 2015, Vol. 51, No 5, pp. 1-8.

6. Kisler J.M., Stevens G.W., O'Connor A.J., 13th Intern. Zeolite Conf., Recent Res. Rep, 18-R-08, Montpellier, Groupe Français des Zéolithes, 2001, pp. 82-91.

7. Zeolites and Mesoporous Materials at the Dawn of the 21ST Century: In Book of Proceedings-Stud. Surf. Sci. Catal. / Ed. by A. Galarneau, F.Di Renzo, F. Fajula, J. Vedrine. Amsterdam; London; New York; Oxford; Paris; Shannon; Tokyo, 2001, Vol. 135, pp. 132-137.

8. Mishra A. et al., Green Materials for Sustainable Water Remediation and Treatment. Royal Society of Chemistry, Cambridge, UK, 2013, 259 p.

9. Khodosova N.A., Belchinskay L.I., Petuchova G.A., Voishevf O.V. , *Protection of Metals and Physical Chemistry of Surfaces,* 2009, Vol. 45, No 6, pp. 722-727.

10. Zhabin A.V., Savko A.D., Ocherki po regopnalnoi geologii, Saratov: Nauka, 2008, pp. 48-56.

11. Wilson M.J., Rock-forming Minerals: Clay Minerals. Sheet silicates. Volume 3C. Geological Society of London, 2013, 724 p.

12. Afanasieva N.I. et al., *Litosphera*, 2013, No 2, pp. 65-75.

13. Novikova L.A. et al., *Sorbtsionnye i khromatograficheskie protsessy,* 2015, Vol. 5, pp. 730-740.

14. Joshi M.S. et.al., *Mater. Chem. Phys.*, 1997, Vol. 48, pp. 187-196.

15. Little L., IR-spectra of adsorption molecules, M., Mir, 1969, 514 p.

16. Mozgawa W., Sitarz M., Rokita M., *J. Mol. Struct.*, 1999, Vol. 512, pp.251-257.

17. Brek D., Zeolite molecular sieves, M.: Mir, 1976, 760 p.

18. White D.A., Bussey R.L., *Separ. Purif. Technol.*, 1997, Vol. 11, pp. 137-141.

19. Karnaukhov A.P. Adsorption. Texture of disperse and porous materials, Novosibirsk, Nauka, Sib.predpriyatie RAN, 1999, 410 p.

20. Kotova D.L. et al., *Nanotechnologies in Russia.*, 2014, Vol. 9, No 9-10, pp. 474-479.

21. Amanollah E., *Adsorption*, 2009, Vol. 15, No 1, pp. 65-73.

22. Greg S., Sing K., Adsorption, specific surface, porosity, M., Nauka, 1970, 407 p.

23. Tarasevich Yu.I., *Ukr. Khim. Jurn.*, 1968, Vol. 34, No 5, pp. 439-446.

Kotova Diana L. – prof., grand Ph.D (chemistry), department of analytical chemistry, Voronezh State University, Voronezh

Krysanova Tatiana A. – Ph.D. (chemistry), associate prof., department of analytical chemistry, Voronezh State University, Voronezh

Belchinskaya Larisa I. – chairwoman of chemistry department, professor, Dr.Sc., department of chemistry, Voronezh State University of Forestry and Technologies named after G.F. Morozov, Voronezh

Artamonova Mariya N. – the student, department of analytical chemistry, Voronezh State University, Voronezh

Novikova Liudmila A. - Ph.D. (chemistry), associate prof., department of chemistry, Voronezh State University of Forestry and Technologies named after G.F. Morozov, Voronezh