

Mechanism of H₂O Vapor Adsorption in A Type Zeolites: A Model Based on Adsorption Calorimetry

Firuz Rakhmatkarieva^{1*}, Odina Davlatova¹, Mirzokhid Kokhkharov¹, Mansur Xudoyberganov¹, Oybek Ergashev¹, Eldor Abdurakhmonov^{1,2}, Tolib Abdulkhaev¹

¹Institute of General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan, 72a, Mirzo Ulugbek str., Tashkent, 100170, Uzbekistan

²Tashkent Institute of Irrigation and Agricultural Mechanization Engineers (TIAME), 39, Kori Niyaziy str., Tashkent, 100000, Uzbekistan

Abstract. In this study, the energy characteristics of water vapor adsorption in NaA and NaA(NaBO₂) zeolites were measured by adsorption calorimetry. Information of differential heats, isotherms, entropy and kinetic of adsorption in the matrix of NaA and NaA(NaBO₂) zeolites were obtained. Adsorption isotherms (a) and differential heats of adsorption (Q_d) of water vapor by NaA and NaA(NaBO₂) zeolites were measured at 303 K. The heats of adsorption are stepwise and each step corresponds to the stoichiometric formation of adsorption complexes of H₂O molecules with Na⁺ or H⁺ ions, (H₂O)_n/Na⁺ or H⁺, (n = 1-4), which are located on the S_{III}, S_{II} and S_I crystallographic positions of NaA and NaA(NaBO₂). Hydration mechanism of NaA and NaA(NaBO₂) are complex and at saturation, the zeolites are occupied by the next water zeolitic host/guest systems: NaA – 2.2[(H₂O)₄/Na⁺_{III}+H⁺], 3[(H₂O)₂/Na⁺_{II}] and 6.6[(H₂O)₂/Na⁺_I]; NaA(NaBO₂) – 2[(H₂O)₄/Na⁺_{III}], 3[(H₂O)₄/Na⁺_{II}] and 6.86[(H₂O)/Na⁺_I]. The complete hydration of the α - and β cages of NaA amounts thus to 21,8 and 6,2 respectively H₂O/u.c. and α -cage of NaA(NaBO₂) – 26,3 H₂O/u.c. The mean molar integral adsorption entropy of water is ~-30,5 J/mol K less than the entropy of the bulk liquid. This value nearly the same as entropy of crystalline water so the mobility of water in the zeolitic matrix is solidlike.

1. Introduction

Over the past several years, interest in zeolite molecular sieves has been increased [1-5]. The widespread use of zeolite type A as desiccant is explained by windows diameter 4.2 Å and adsorption properties. Different forms of H₂O molecules bond in A type zeolite exist [6-9]. However, data [10] of uniformity of “zeolite water” is also available. Unfortunately, a detailed study has not yet been carried out in all areas of filling of either the adsorption isotherms or the heats of water adsorption on this practically important adsorbent. The available data for adsorption isotherms, as a rule, refer to high degrees of filling, since experts in the field of adsorption have not yet overcome the difficulties of precision measurements of low equilibrium water vapor pressures (10⁻¹⁰ torr). As regards the published data for the differential heats of adsorption of water on NaA [11, 12], they are either limited only to average occupancies [11] or unreliable [12] due to the long establishment of equilibrium states.

A breakthrough in calorimetric studies of adsorption in zeolites for systems with a long “main period” of the calorimetric experiment was made in [13] study of water adsorption in NaA crystalline zeolite. Two kinds of adsorption centers were found to differ sharply in terms of energy. However, precise detailing of the energy of this process in the entire region of filling was impossible on the equipment used in [13], although extremely rich information was obtained regarding the dynamics of adsorption. In this regard, we decided to make an attempt to return to this system, but using a more high-precision adsorption-calorimetric setup described in [14, 15], in order to obtain more detailed information about the structure of ion-molecular complexes in the zeolite matrix and the patterns of adsorption polar water molecule at various stages of filling its cavities.

2. Materials and Methods

Differential molar adsorption calorimetric studies of water adsorption in NaA zeolite were carried out using the device described in [14, 15, 18]. The use of the method of compensation of heat fluxes by the Peltier effect made it

*Corresponding author: rakhfiruza@gmail.com

possible to increase the accuracy of measuring the heat of adsorption. Adsorption measurements were carried out on a unique high-vacuum volumetric setup, which made it possible to carry out adsorption measurements and dosing of the adsorbate with high accuracy.

The NaA zeolite used for this study is a synthetic binder-free zeolite. Zeolite NaA(NaBO₂) was obtained by the hydrothermal method [16] and kindly provided by Dr. J.C. Buhl from the University of Hannover. Before the inlet of water vapor, the sample was warmed up and subjected to high-vacuum pumping at 450°C for 10 hours. Before measurements, the water was carefully purified.

3. Results and Discussion

Figure 1 shows the adsorption isotherms at 303K of water in NaA (1) and NaA(NaBO₂) (2) extending to $\sim 10^{-6}$ of relative pressure p/p^0 (p^0 is the vapor pressure of water, p^0 (303 K) = 4.24 kPa, Handbook of Chemistry and Physics, 1975 [17]). The adsorbed amount, expressed in the unit H₂O per unit cell (u.c.), was calculated from the experimentally determined quantity a /mmol according to $N/\text{H}_2\text{O}$ per u.c. = ka /mmol/g with $k = 1,7$ and $1,77$ for NaA and NaA(BO₂), respectively, taking into account the differently molar masses. Starting with a convex shape, the adsorption isotherms rise steeply from $\sim 12,92$ to $\sim 21,93$ water molecules per unit cell (u.c.) ($\sim 7,6$ to $\sim 12,9$ mmol/g) (1) and from $\sim 8,32$ to $\sim 19,29$ H₂O/u.c. ($\sim 4,7$ to $\sim 10,9$ mmol/g) (2). Then curves sharply turn toward the ordinate and increase linearly up to saturation.

Figure 2 shows the differential heat of adsorption, Q_d , at 303 K of water in NaA and NaA(NaBO₂) as a function of the amount adsorbed. For NaA, Q_d , (fig 2, 1) starts at about 110 kJ/mol and decreases to 99,2 kJ/mol at 1,58 H₂O u.c. ($a = 0,93$ mmol/g). Subsequently, Q_d , forms a high energetic step from 99,2 to 66 kJ/mol in the interval of adsorption from 1,58-5,3 H₂O u.c. (0,93-3,12 mmol/g). Further adsorption is followed with formation of several well-defined steps or waves in the interval of N from 5,3 to 8,4 H₂O u.c. (3,12 to 4,94 mmol/g) with Q_d changing from 66,1 to 65,51 kJ/mol; then N 8,4-10,52 H₂O u.c. (4,94-6,19 mmol/g), Q_d 65,51-65,34 kJ/mol; N 10,52-17,1 H₂O u.c., (6,19-10,06 mmol/g), Q_d 65,34-66,94 kJ/mol; $N = 17,1-23,3$ H₂O u.c. (10,06-13,71 mmol/g), Q_d 66,94-62,42 kJ/mol; N 23,3-25,67 H₂O u.c. (13,71-15,1 mmol/g), Q_d 62,42-56,28 kJ/mol; N 25,67-27,81 H₂O u.c. (15,1-16,5 mmol/g), Q_d 56,28-43,5 kJ/mol N 27,81-28,0 H₂O u.c. Dashed line is the heat of vaporization of water at 303 K ($\Delta_v H$ kJ/mol = 43,5 kJ/mol).

Generally in the case of NaA(BO₂), Q_d (fig 2, 2) on 15 kJ/mol lays lower, Q_d of NaA. A sharp initial decrease is not observed. Instead of this we see a high energetic step with wider plateau at ~ 95 kJ/mol and then, Q_d , drops sharply to 62 kJ/mol when $N = 5,1$ H₂O u.c. As in the case of NaA further adsorption is followed with formation of several steps or waves in the intervals of N from 5,1 to 7,1 H₂O u.c. with Q_d changing from 61,9 to 61,95 kJ/mol; then N 7,1-10,73 H₂O u.c., Q_d 61,95-60,29 kJ/mol; N 10,73-13,59 H₂O u.c., Q_d 60,29-62,11 kJ/mol; N 13,59-15,55 H₂O/u.c., Q_d 62,11-61,6 kJ/mol; N 15,55-21,7 H₂O u.c., Q_d 61,6-52,4 kJ/mol; N 21,7-25,31 H₂O u.c., Q_d 52,4-44 kJ/mol; N 25,31-26,3 H₂O/u.c. Dashed line is the heat of vaporization of water at 303 K ($\Delta_v H$ kJ/mol = 43,5 kJ/mol).

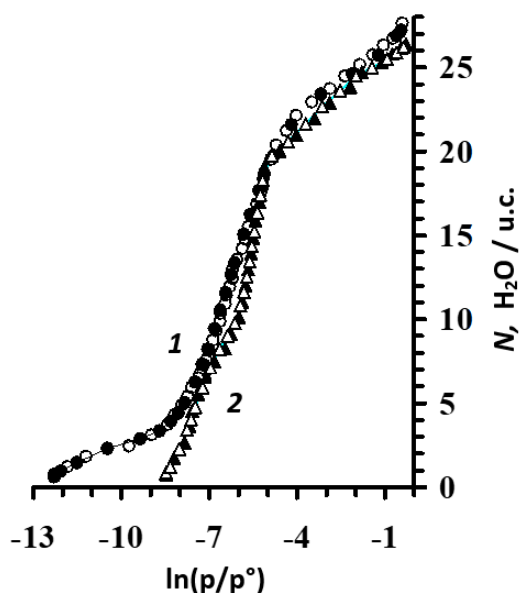


Fig. 1. Isotherm of H₂O adsorption in zeolites 1 - NaA, 2 – NaA (NaBO₂) at 303 K. ○, △- experimental data; ●, ▲-calculated using VMOT

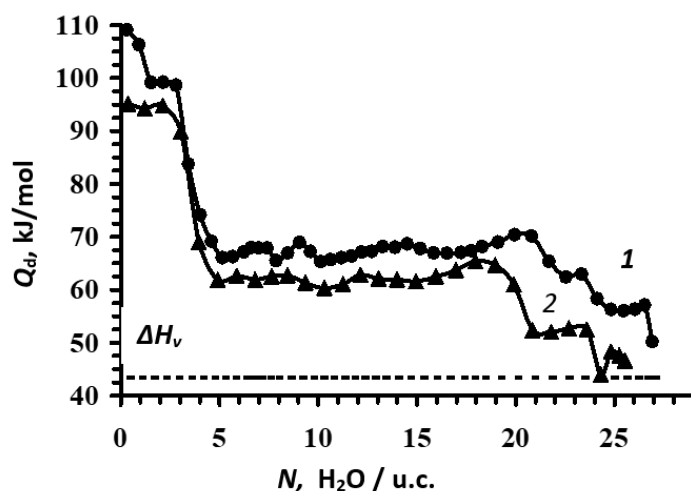


Fig. 2. Differential heats of adsorption, Q_d , of H_2O at 303 K in NaA (1) and NaA(NaBO₂)(2). The dashed line represents the heat of vaporization of bulk water at 303 K, $\Delta H_v = 43.5$ kJ/mol

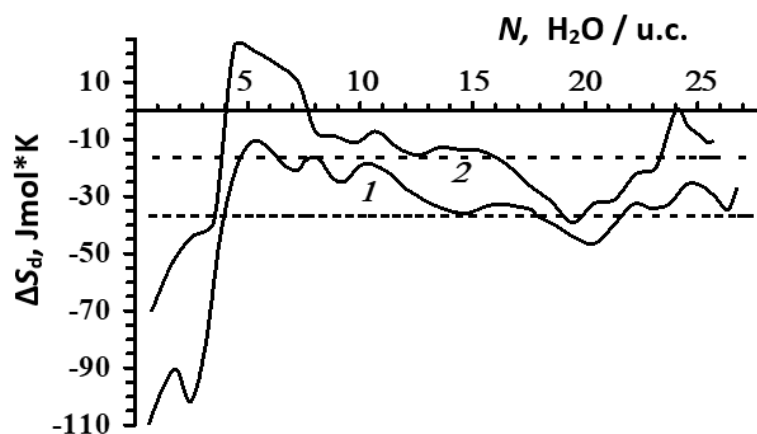


Fig. 3. Differential entropy of adsorption, ΔS_d , of H_2O at 303 K in NaA (1) and NaA(NaBO₂) (2). The entropy of the bulk liquid was taken as being equal to zero

Figure 3 shows the molar differential adsorption entropy (ΔS_d) of water in zeolites NaA(1) and NaA(NaBO₂) (2). The entropy of the bulk liquid was taken as being equal to zero. In general, the ΔS_d curves are located below the entropy of liquid water, except for a small section in the α range from 4 to 7.5 H₂O/u.c. in zeolite NaA(NaBO₂). In accordance with the shape of the curve of differential heats of adsorption, the entropy of water adsorption in NaA, starting from -110 J/mol*K, rapidly increases to -5.4 J/mol*K at 5 H₂O/u.c., then smoothly and wavy decreases to 20 H₂O/u.c., after which also grows in waves until the zeolite is saturated with water. A deep minimum at low fillings indicates a strong localization of water molecules on the H⁺, Na_{III}, and Na_{II} cations. The average molar integral entropy of water adsorption in the NaA zeolite is lower than the entropy of ice and is equal to -36.8 J/mol*K, which indicates a significant loss of mobility of water molecules in NaA zeolite matrix up to its complete localization. The curve of the molar differential entropy of water adsorption in NaA(NaBO₂) zeolite generally follows the ΔS_d curve of the H₂O-NaA system and is located higher. The average molar integral entropy of water adsorption in NaA(NaBO₂) is also higher and amounts to -16.5 J/mol*K. The mobility of water molecules in the NaA(NaBO₂) zeolite matrix is somewhere between the mobility of water and ice.

Figure 4 shows the time to establish adsorption equilibria, τ , of H₂O at 303K in NaA (1) and NaA(NaBO₂) (2). For NaA, starting from ~11.5 hours, the curve decreases in waves to 2 hours at $N = 10.35$ H₂O/u.c., and remains almost constant with two waves with a maximum at 13.56 and 20.38 H₂O/u.c. The second wave decreases to $\tau = 1.6$ hours at $N = 22.14$ H₂O/u.c. Finally, according to the last two steps on the Q_d curve, τ remains almost constant at 1.5 h, then drops to 1 h. In the case of NaA(NaBO₂) τ passes through a maximum (7.35 hours) at $N = 2.69$ H₂O/u.c., then decreases monotonically to 10.21 H₂O/u.c. (1.6 hour) and stabilizes at this level to 25 H₂O/u.c.

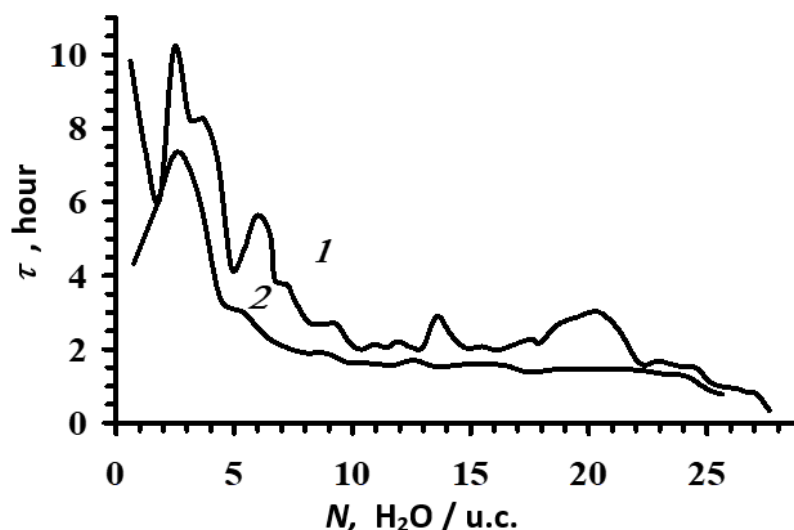


Fig. 4. The time to establish adsorption equilibria, τ , of H_2O at 303 K in NaA (1) and NaA(NaBO_2) (2)

4. Conclusion

Formation of a four-dimensional complex with H^+ and Na^+ cations in position S_{III} on the τ curve in the range from 8.14 to 10.12 $\text{H}_2\text{O}/\text{u.c.}$ characterized by a slowdown in the adsorption process. The section responsible for water adsorption in β -cavities is characterized by a small maximum at the moment of completion of adsorption in β -cavities. The difficulties experienced by a water molecule to overcome the barrier of 80 kJ/mol when penetrating through a six-membered oxygen ring in the β -cavity are clearly seen in our earlier work [13]. The relatively large weight of two samples of the studied NaA zeolites (3.7 and 4.5 g) greatly slowed down the process of processing the charge with water, especially at low fillings (200–350 hours respectively). At large fillings, the process accelerated (30–40 hours), but in the region of adsorption in β -cavities, the time for establishing adsorption equilibrium τ began to slow down again and reached 65–90 hours.

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References

1. P. Demontis, J. Gulín-González, H. Jobic, M. Masia, R. Sale, G.B. Suffritti, Dynamical Properties of Confined Water Nanoclusters: Simulation Study of Hydrated Zeolite NaA: Structural and Vibrational Properties, *ACS Nano* **2**(8), 1603-1614 (2008)
2. P. Demontis, J. Gulín-González, M. Masia, G.B. Suffritti, The behaviour of water confined in zeolites: molecular dynamics simulations versus experiment, *Journal of Physics: Condensed Matter* **22**, 284106 (2010)
3. A. Mikula, M. Krol, A. Kolezyaski, The influence of the long-range order on the vibrational spectra of structures based on sodalite cage, *Spectrochem. Acta A Mol. Biomol. Spectros* **144**, 273-280 (2015)
4. H. Sun, D. Wu, X. Guo, B. Shen, A. Navrotsky, Energetics of sodium-calcium exchanged zeolite A, *Phys. Chem. Chem. Phys.* **17**(17), 11198-111203 (2015)
5. E. Csanyi, Z. Hato, T. Kristof, Molecular simulation of water removal from simple gases with zeolite NaA, *Mol. Model* **818**(6), 2349-2356 (2012)
6. D.W. Breck, W.G. Eversole, R.M. Milton, T.B. Reed, *J. Amer. Chem. Soc.* **78**, 5963-5972 (1956)
7. G.J.S. Frohnsdorf, G.L. Kington, *Proc. Roy. Soc.* **A247**, 469 (1958)
8. G.V. Yikhnevich, E.E. Senderov, *Geochemistry* **1**, 48 (1963)
9. J.V. Smith, F. Rinaldi, L.S. Denet-Glasser, *Acta Crystallogr.* **16**, 45 (1963)
10. S.P. Gabuda, *Sat. Zeolites, their synthesis, properties and applications*, Science, Moscow (1965)
11. G.L. Kington, *The structure and Properties of Porous Materials*, Butterworths publ., London (1958)
12. N.N. Avgul, A.V. Kiselev, Ya.V. Mirsky, M.V. J. Serdobov, *Physical chemistry* **42**, 1474 (1968)

13. M.M. Dubinin, A.A. Isirikyan, G.U. Rakhmatkariev, V.V. Serpinsky, Energy of adsorption of gases and vapors on microporous adsorbents. Message 3. Differential heats of adsorption of water on crystalline synthetic zeolite NaA, *Izv. USSR Academy of Sciences Ser. Chem.* **4**, 1269-1276 (1972)
14. B.F. Mentzen, G.U. Rakhmatkariev, Host/Guest interactions in zeolitic nonstructured MFI type materials: Complementarity of X-ray Powder Diffraction, NMR spectroscopy, Adsorption calorimetry and Computer Simulations, *UZB. chem. log.* **6**, 10-31 (2007)
15. G.U. Rakhmatkariev, Mechanism of Adsorption of Water Vapor by Muscovite: A Model Based on Adsorption Calorimetry, *Clays and Clay Minerals* **54**, 423-430 (2006)
16. Ch. Gurriss, D. Reich, J.Ch. Buhl, W.W. Hoffman, Synthesis and properties of zeolite A with salt-containing β -cages, *Stud. Surf. Sci. and Catal.* **98**, 46-47 (1995)
17. R.C. Weast, Handbook of Chemistry and Physics, CRC Press, Cleveland (1975)
18. E. Abdurakhmonov, I.B. Sapaev, B. Abdullaeva, F. Rakhmatkarieva, N.N. Dekhkanova, Thermodynamics of hydrogen sulfide adsorption in Zeolite LiX, *E3S Web of Conferences* **383**, 04018 (2023)