DIFFERENTIAL ENTROPIES OF WATER ADSORPTION IN ZEOLITE NH$_4$ZSM-5

Abdulkhaev T.D. (Republic of Uzbekistan)
Email: Abdulkhaev515@scientifictext.ru

Abdulkhaev Tolibjon Dolimjonovich - Doctoral Student,
DEPARTMENT CHEMICAL TECHNOLOGY,
NAMAGAN ENGINEERING AND TECHNOLOGY INSTITUTE,
NAMAGAN, REPUBLIC OF UZBEKISTAN

*Absract: differential entropies and thermokinetics of water adsorption in the NH$_4$ZSM-5 zeolite were measured at 303K. The detailed mechanism of water adsorption in NH$_4$ZSM-5 zeolite from zero filling to saturation was discovered. The isotherm of adsorption was quantitatively reproduced on the basis of VOM theory. The average molar integral entropy of water adsorption in NH$_4$ZSM-5 zeolite is lower than the ice entropy and is – 43.54 J / mol * K, which indicates a significant loss of mobility of water molecules in NH$_4$ZSM-5 zeolite matrix up to its full localization. The time to establish adsorption equilibrium (τ) in the H2O-NH$_4$ZSM-5 system at low fillings is strongly slowed down and reaches 12–10 hours, at large fillings it decreases to 30 minutes.*
Keywords: entropies, thermokinetics, NH$_4$ZSM-5 zeolite, water, adsorption calorimetry.

ДИФФЕРЕНЦИАЛЬНАЯ ЭНТРОПИЯ АДСОРБЦИИ ВОДЫ В ЦЕОЛИТЕ NH$_4$ZSM-5
Абдулхаев Т.Д. (Республика Узбекистан)

Абдулхаев Толибжон Долимжонович - базовый докторант,
кафедра химической технологии,
Наманганский инженерно-технологический институт,
г. Наманган, Республика Узбекистан

*Аннотация: дифференциальные энтропия и термокинетика адсорбции воды в цеолите NH$_4$ZSM-5 были измерены при 303K. Раскрыт детальный механизм адсорбции воды в цеолите NH$_4$ZSM-5 от нулевого заполнения до насыщения. Изотерма адсорбции полностью описывается уравнением ТОЗМ. Среднемольная интегральная энтропия адсорбции воды в цеолите NH$_4$ZSM-5 ниже энтропии льда и равна – 43,54 Дж/моль*К, что указывает на существенную потерю подвижности молекул воды в матрице цеолита NH$_4$ZSM-5 вплоть до полной её локализации. Время установления адсорбционного равновесия (τ) в системе H2O-NH$_4$ZSM-5 при малых заполнениях сильно замедленно и достигает 12–10 часов, при больших заполнениях оно доходит до 30 минут.*

Through adducing the physicochemical, especially energy characteristics of zeolite ZSM-5, one can learn about the theoretical and practical significance of zeolite. Studying the energy properties of zeolites makes it possible to know their chemical composition and crystal structure, and this, in turn, makes it possible to use them as a reference in practical calculations and theoretical discussions. From this it follows that the classification of the thermodynamic values of the adsorption of various adsorbates to some zeolites is required.

To study the physical-chemical properties of adsorption on zeolites, first of all, it is necessary to conduct a precise measurement of the total thermodynamic properties of adsorption using the calorimetric method in a high-vacuum adsorption-microcalorimetric installation [1]. The installation consists of heat-resistant glass tubes intended for high-vacuum devices, capillary microburettesand mercury closures, as well as adsorbent ampoules, measuring parts, segregations for storing adsorbents, sections for gas and steam preparation, and pump systems intended to form a vacuum.

As an object of study, defect-free zeolites of the ZSM-5 type with a high concentration of ammonium cations synthesized in a fluorine medium were selected. Initially,by an analytical balance 0.2 g. of adsorbent is weighed in the form of a powder, the dimensions of which do not exceed 1 mm., then finely granulated the zeolite under a pressure of 4 t. is re-measured on a balance. The zeolite suspended on the scales is placed in an ampoule (the ampoule also needs to be weighed). The ampoule with zeolite is placed in an even larger ampoule and is adjusted in the installation for the formation of vacuum. The installation is heated and pumped out for 8 hours at a predetermined temperature of 450°C until a vacuum is formed, i.e. until a pressure of 10^{-4} Pa is reached. [2]

As shown in the literature [3], in the zeolite NH₄ZSM-5 at 303 K, the differential heat and isothermal values of water adsorption are calculated. From these values, the differential molar entropy of adsorption is calculated. The isothermal value of adsorption, in turn, is compared by the equation of the theory of micropore volumetric filling (VOM).
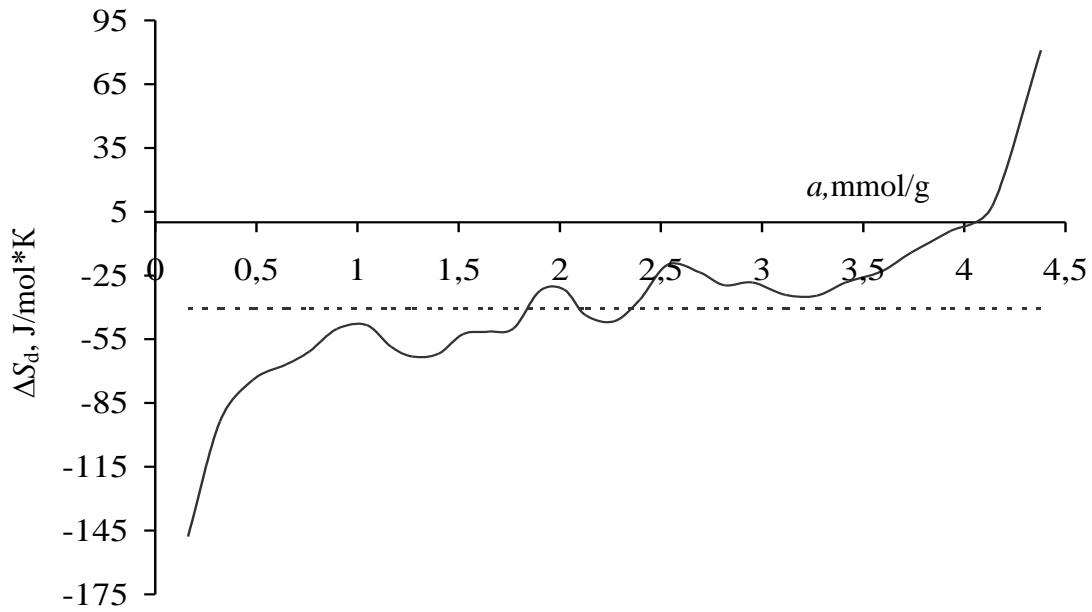
Fig. 1. Differential entropies of water adsorption in zeolite NH₄ZSM-5 at 303K

According to the Gibbs-Helmholtz equation, the molar differential entropy of water adsorption (ΔS_d), isotherms and adsorption-differential heats are calculated as follows:

$$\Delta S_a = \frac{\Delta H - \Delta G}{T} = \frac{-(Q_a - \lambda) + A}{T} \qquad (2)$$

where-λ is the heat of condensation, ΔH and ΔG are the change in free energy and enthalpy in adsorption process during the transition from the standard position to the adsorption position.
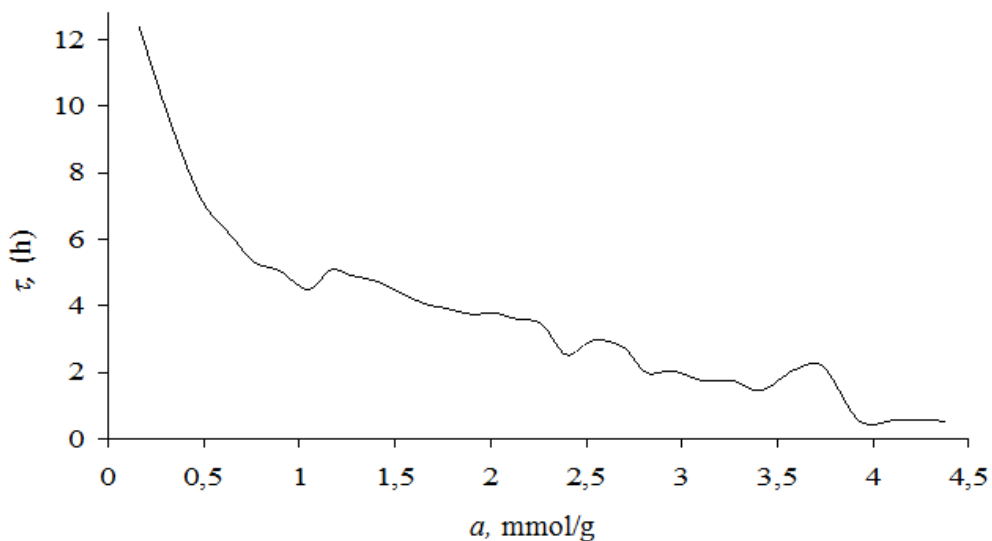
Fig. 2. The time of establishment of adsorption equilibrium, τ, as a function of the adsorption of water in NH$_4$ZSM-5 at 303K

The entropy diagram is shown in fig. 3. A sharp increase in the molar differential entropy of water adsorption-150 is given at 50 J / mol * K, i.e., from the minimum value to the maximum value, this, as mentioned above, is the adsorbed primary water molecules in the zeolite channels freely form an ion-molecular tetra-aqua complex with active centers of ammonium, and in this regard, the curve of the entropy line is located below the entropy of liquid water. With an increase in this saturation value, the entropy value sharply increases from liquid entropy to vapor entropy.The average values of the entropy integral are correspondingly much smaller than the liquid value - 43.54 J / mol * K. Thus, differential and integral entropy in zeolite show the state of motion of each adsorbed water molecule.

The establishment of the adsorption equilibrium of water molecules in the context of zigzag and direct channels in the NH$_4$ZSM-5 zeolite (to 0.98 mmol / g) gradually decreases, and then rapidly grows.In this case, the equilibrium time decreases from 12.2 hours to 4.1 hours. In primary adsorption, it takes more time for a strong bond of water molecules with active centers.In the following stages, it takes less time to bind water molecules with hydrogen (3-4 hours), and to bind the adsorbate-adsorbate (1.2 hours).Atthe last stage, a decrease in the time to establish adsorption equilibrium to 30–40 minutes is explained by the conservation of a pair of water molecules due to the interaction of fully adsorbed molecules in non-adsorbed molecules in the adsorption volume.

One can also judge from the heat of adsorption and the isotherm that NH$_4$ZSM-5 zeolite has organophilic properties.The detailed mechanism of water adsorption in NH$_4$ZSM-5 zeolite from zero filling to saturation was discovered. The isotherm of adsorption was quantitatively reproduced on the basis of VOM theory.

References / Список литературы

1. *Dubinin M.M., Rakhmatkariev G.U., Isirikyan A.A.* // "Izvestia Akademii Nauk" USSR. Ser. chem., 1989. № 9. P. 2117.
2. *Yakubov Y.Yu.* Thermodynamics of the formation of ion-molecular complexes in zeolites HZSM-5 // Izv. diss. cand, 2017. Pp. 39-50.
3. *Rakhmatkariev G.U.* Mechanism of Adsorption of Water Vapor by Muscovite: A Model Based on Adsorption Calorimetry // Clays and Clay Minerals, 2006, Vol. 54. Pp. 423-430.