

## INFLUENCE OF THE TEMPERATURE ON THE FORM OF THE DEPENDENCE OF HEAT OF ADSORPTION OF WATER BY ZEOLITE KNaX ON THE ADSORPTION AMOUNT\*

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Dependence of differential heat of adsorption of water vapour on the amount adsorbed by zeolite KNaX at different temperatures was determined calorimetrically. With the temperature rising the wave-shaped nature of the corresponding curves becomes flattening, maxima and minima disappear, indicating the more uniform distribution of water molecules on energetically different sites zeolite cavities. Obtained from this data dependence of heat capacity of adsorbed water on the amount of adsorption is close to that measured directly and is also flattened with the rise in temperature.

Dependence of differential heat of adsorption  $\bar{q}_v$  of water vapour by zeolite KNaX at 23°C on the amount of adsorption  $n^s$  is wave-shaped in nature<sup>1</sup>. It is caused by predominately successive adsorption of water molecules, at first mostly on cations, and, then, mainly on the ribs of the framework of zeolite, and, at last, in the medium part of the cavities. At all these stages a sufficient role is played by development of hydrogen bonds of water molecules with the frame-work of zeolite and between each other. Spectroscopic research<sup>2</sup> revealed that the energy of hydrogen bonding is changed depending on  $n^s$ . Dependence on  $n^s$  of heat capacity of water-zeolite KNaX system is also of wave-shaped nature<sup>3</sup>. It points to the molecular transfers taking place in this system and to strong temperature dependence of  $\bar{q}_v$ .

In the present paper measurements of dependence of  $\bar{q}_v$  of water on  $n^s$  with the same zeolite KNaX in an isothermal double calorimeter at different temperatures are given.

Liberation of the heat of adsorption in zeolite-water system at low temperatures is a very slow process. Tens and hundreds of hours are required for its completion at low  $n^s$ . In this connection the possibility of obtaining thermal equilibrium by studying kinetics of heat liberation was examined. These kinetics can be approximated by asymptotic equation  $\bar{q}_{v,t} = \bar{q}_v [1 - \exp(-bt)]$ . If we register dependence of

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$\bar{q}_{v,\tau}$  on  $\tau$  long enough, then, having used, for instance, regression analysis, we can find  $\beta$  and ultimate (equilibrium)  $\bar{L}_v$  value. Analysis of kinetic curves of a number of calorimetric adsorption measurements at different  $n^s$  showed that a simpler equation  $\bar{q}_{v,\tau} = \bar{q}_v + b\tau^{-n}$  can be used, which makes easier the fitting of parameters of kinetic equation at relatively simple computers. This method is acceptable if enough number of measurements of  $\bar{q}_{v,\tau}$ ,  $\tau$  can be done with lesser expenses than direct determination of ultimate  $\bar{q}_v$  value. This method of determination of  $\bar{q}_v$  allowed to cut down the time for calorimetric measurement at low  $n^s$  and at 23°C. The results

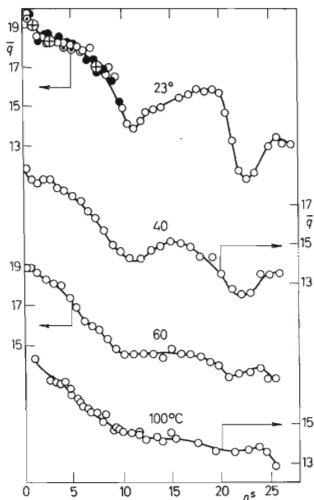


FIG. 1

Dependences of Differential Heat of Adsorption  $\bar{q}_v$  (kcal mol<sup>-1</sup>) of Water on the Amount of Adsorption  $n^s$  (molecules per cavity) by KNaX Zeolite at Different Temperatures (indicated at the curves)

Crosses indicate the  $\bar{q}_v$  value obtained from the analysis of the heat kinetics.

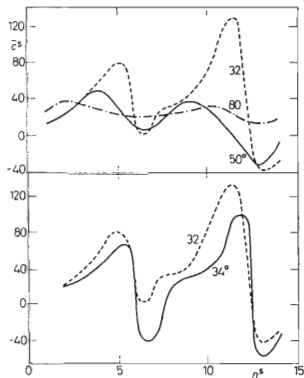


FIG. 2

Dependences of Differential Heat Capacity  $\bar{c}^s$  (cal.mol<sup>-1</sup>.K<sup>-1</sup>) of Adsorbed Water on the Amount of Adsorption  $n^s$  (molecules per cavity) by KNaX Zeolite of Different Temperatures (indicated at the curves)

Solid curve below was calculated from direct calorimetric measurements of heat capacity<sup>3</sup>.

obtained coincided with  $\bar{q}_v$  values, measured in prolonged tests. In Fig. 1 the results obtained from this treatment of kinetic curves are marked by crosses.

Fig. 1 shows dependence of  $\bar{q}_v$  of water on  $n^s$ . At 23°C and  $n^s \approx 8$  molecules per cavity, in main, the development of small bridges of water molecules, between cations and oxygen frame-work of zeolite at  $\bar{q}_v \approx 19$  kcal/mol, has already completed. Then,  $\bar{q}_v$  passes minimum (about 13 kcal/mol) since water molecules did not find such advantageous sites for adsorption. Further increase in  $\bar{q}_v$  to 16 kcal/mol is connected, mainly, with completion of layer formation of associated water molecules on the zeolite ribs (at about 20 water molecules per cavity). Further adsorption starts at considerably lower  $\bar{q}_v \approx 11$  kcal/mol. Continuation of increase of  $n^s$  brings about the development of hydrogen bonds in medium not-filled part of zeolite cavities, and  $\bar{q}_v$  increases again by 2–3 kcal/mol.

Comparison of water molecule size, probable distances between the cations, sizes of ribs and cavities of zeolite framework allows to find the correspondence of curve to mainly successive stages of filling of zeolite cavity at 23°C.

Fig. 1 shows that as the temperature increases maxima and minima on the curve of dependence of  $\bar{q}_v$  on  $n^s$  disappear. It is connected with the fact that at higher temperatures water-zeolite and water-water intermolecular interactions localize adsorbed molecules less definitely, as a result of which, filling of cavities is more uniform.

From the heat curves shown in Fig. 1 it is possible to obtain the dependence of differential heat capacity  $\bar{c}^s$  of adsorbed water on  $n^s$  for three intermediate temperatures: 32, 50 and 80°C. Fig. 2 shows that curve 1, measured by this method, is close to curve 2, obtained from direct measuring<sup>3</sup> of heat capacity of zeolite KNaX-H<sub>2</sub>O system at similar temperature. Positions of maxima and minima on these curves and on curves 1–3 in Fig. 1 are close. The maxima on heat capacity curves correspond to primary completion at lower temperatures of formation of some associated structures of water molecules and to initial formation of other associated structures. At higher temperatures for  $\bar{C}^s$ , as well as for  $\bar{q}_v$ , smoother dependence on  $n^s$  takes place.

For final interpretation of data obtained by all these methods, the information is required about the influence of adsorbed water upon the cation position at different  $n^s$  and at different temperatures, and corresponding molecular-statistical treatment as well.

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