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Abstract

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MOLECULAR SIEVES AS ADSORBENTS OF THE 1st STRUCTURAL TYPE

Porous crystals obtained by removing water from natural or synthetic zeolites have long attracted the attention of researchers. An extensive literature is devoted to the study of the adsorption properties of these crystals. In recent years interest in these sorbents has greatly increased in connection with their practical application, since their uniform porosity of molecular dimensions makes it possible to carry out a very sharp separation of mixtures of substances; moreover, the mechanism of the separation process makes it fully justified to call zeolites molecular sieves. Extensive studies by Barrer and his co-workers (see, for example, (1)) have clarified many features of the adsorption properties of zeolites and have made it possible to classify molecular sieves on the basis of their X-ray structural and sorption characteristics.

The porous sorbents most important in practical terms can be arranged in order of decreasing pore size, which to a certain extent determines their sorption properties. In such a series (large-pore silica gels, activated carbons of the 2nd structural type, small-pore silica gels, activated carbons of the 1st structural type, zeolites), the extreme position on the right is occupied by zeolites, both in terms of the sizes of their pores (structural cells) and, especially, in terms of the sizes of the openings (“windows”) leading into these cells.

Despite numerous attempts at a theoretical analysis of adsorption phenomena, there still does not exist a unified theory that would make it possible to describe quantitatively the adsorption equilibrium for all these types of sorbents. Moreover, even for some particular adsorbent, none of the existing theories makes it possible, under specified conditions, to predict the adsorption equilibrium from known characteristics of the adsorbent and the adsorbed substance. The only exception is the potential theory of adsorption in its present state (2), since, at least for activated carbons of the 1st structural type, it makes it possible to solve this problem over a broad range of variation of the variables with an accuracy sufficient for most practical purposes.

Fig. 1

Figure 1: Fig. 1

As is known, the equation of the adsorption isotherm derived on the basis of the potential theory (3) can be written in the following form

$$\lg a = \lg \frac{W_0}{v} - \frac{0.43\, BT^2}{\beta^2} \lg^2 h, \tag{1}$$

which gives a linear relationship between the logarithm of adsorption a and the square of the logarithm of the relative pressure $h = p/p_s$. This equation describes well the extensive experimental material on the adsorption of various substances on activated carbons of the 1st structural type and small-pore silica gels (4), and makes it possible, from the constants W_0 and B, determined from the adsorption isotherm of a standard substance (for example, nitrogen at −195° or benzene at 20°), to predict, over a wide temperature range, the adsorption equilibrium for other substances on a given adsorbent from tabulated values of the molar volume v, the affinity coefficient of the characteristic curve β, and the saturated-vapor pressure p_s of these substances. Since zeolites may be regarded as a limiting member of the indicated series of porous sorbents, it is natural to try to establish to what extent equation (1) is applicable for a quantitative description of adsorption on zeolites. To clarify this question, we plotted the experimental data available to us and some data known from the literature in the coordinates of equation (1), and obtained satisfactory linear dependences between $\lg a$ and $\lg^2 h$, as shown in Fig. 1. Straight line 1 represents the adsorption isotherm of nitrogen vapor at −195° on the molecular sieve "Linde 5A," measured by us by the weight method (5); curves 2 and 3 represent, respectively, the isotherms of adsorption of nitrogen and argon on chabazite at −183°, constructed by us from the tabulated data given in the paper of Barrer and Robins (6). In all three cases equation (1) is well obeyed over the entire interval studied. It should be noted that the adsorption isotherms of argon on natural and calcium chabazite, measured in (7), are described by this equation only over an interval of three orders of pressure (from $h \approx 1 \cdot 10^{-4}$ and higher), while in the region $h < 1 \cdot 10^{-4}$ considerable deviations from linearity are observed. Leaving open the question of the cause of these deviations, we wish to emphasize that, in the case of such steep adsorption isotherms, the kinetics of establishment of equilibrium is often very greatly prolonged, and therefore measurements of small equilibrium pressures in the initial part of the isotherm cannot be sufficiently reliable.

Fig. 1

Thus, from our point of view, one may speak of a satisfactory applicability of equation (1) to the adsorption of vapors of substances on zeolites approximately in the same range of relative pressures as in the case of adsorption on active carbons of the 1st structural type, at least for those substances whose adsorption is mainly determined by dispersion forces. If, from curves 2 and 3 in Fig. 1, the constants W_0 and B are calculated, taking nitrogen as the standard substance ($\beta = 1$) and determining β for any other substance as the ratio of the parachor of this substance to the parachor of nitrogen, then the values of W_0 for argon and nitrogen prove to be 0.192 and 0.217 cm^3/g, and the corresponding values of B are 1.47 and $1.51 \cdot 10^{-6}$ (if benzene is chosen as the standard substance, the values of B are 0.160 and $0.165 \cdot 10^{-6}$). For nitrogen, in view of the closeness of the experimental temperature to the critical temperature, the molar volume in the adsorbed state at -183° ($v = 35.7\ \mathrm{cm}^3/\mathrm{mol}$) was estimated by the method described in ([8]). The values of B found in this way agree well with one another; the values of W_0 differ from one another by about 12%.

To judge to what extent equation (1) permits prediction of the adsorption equilibrium of other substances on zeolites from the constants W_0 and B, characterizing the given adsorbent and determined on the basis of one adsorption isotherm of a standard substance, and from tabulated values of the constants of the adsorbed substances, we calculated the adsorption isotherms of methyl chloride at three temperatures: 0, 50, and 100° on chabazite, and compared the calculated isotherms with direct measurements of adsorption of this substance on natural chabazite, given in the paper of Barrer and Brook ([9]). For these calculations we adopted the indicated values $W_0 = 0.217\ \mathrm{cm}^3/\mathrm{g}$ and $B = 1.51 \cdot 10^{-6}$, determined from the adsorption isotherm of nitrogen ([6]), and the required values of the molar volume v of methyl chloride

in the adsorbed state at these temperatures was estimated by the method set forth in (8), by linear interpolation between the value of v at the boiling temperature and the value of the van der Waals constant b at the critical temperature. The affinity coefficient of the characteristic curve β was obtained from the corresponding coefficient for ethyl chloride, with a correction for the parachor increment for the CH_2 group, and the saturated vapor pressures of CH_3Cl were calculated from tabular data (10). The results of the calculations are presented in Fig. 2 by solid lines in the form of adsorption isotherms of CH_3Cl on chabazite for temperatures of 0, 50, and 100°, with equilibrium pressures in millimeters of mercury plotted on the abscissa and adsorption values in millimoles per gram on the ordinate. The circles in this figure show the experimental points found by Barrer and Brook (9) at the same temperatures. For the isotherm at 50°, very good agreement is observed between the measured and calculated adsorption values. The experimental points at 100° lie somewhat lower, and at 0° somewhat higher than the calculated isotherm; however, the largest deviations in both cases do not exceed 5%. The agreement between the calculated and measured adsorption values proves to be even somewhat unexpectedly good, if one takes into account that the calculations of CH_3Cl adsorption were carried out in the interval from 0 to 100° using the adsorption isotherm of N_2, measured at -183°; that the method used to estimate the molar volume of the substance in the adsorbed state is inevitably approximate; and, finally, that the adsorbents used in (6,9) may have differed somewhat from one another. On the basis

Fig. 2

Figure 2: Fig. 2

of the foregoing, one may think that the affinity coefficients determined from adsorption isotherms on carbons and expressed through the ratio of parachors retain their values in the transition to adsorption on zeolites.

Fig. 2

We also note that our calculations of the total heat of adsorption of CH_3Cl on chabazite using the same values of W_0 and B at $a = 3$ mmol/g, according to the equation derived on the basis of the potential theory of adsorption (see (11), equation (7)), led to a value of 11.5 kcal/mol, as compared with the value 14.7 found by Barrer and Brook (9), at approximately the same adsorption value, from the Clapeyron–Clausius equation.

From our point of view, the results presented here of preliminary calculations indicate the advisability of applying equation (1) in the study of adsorption on zeolites (with the aim of clarifying the range of applicability and possible limitations) and make it possible to regard molecular sieves as adsorbents of the first structural type, to which, to a greater or lesser degree, the computational apparatus of the potential theory being developed in recent years in our laboratory is applicable.

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