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Separation of Binary Solutions on the Basis of Zeolites

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Abstract

In this chapter, the author analyzed binary systems, ethanol + water, methanol + water and benzene + water, and an original mathematical model allowing the determination of the complete adsorption of binary systems on KaA, CaA, CaX, NaA and NaX zeolites using the Gibbs adsorption theory is proposed. The Gibbs equation and the Gibbs-Duhem equation have a number of limitations and do not take into account the properties of the investigated zeolites. Therefore, it is necessary to use the equations obtained by the author as a result of laboratory research, for the theoretical calculation and development of dehydration and concentration systems for alcohols.

Keywords: zeolites, binary solutions, molecular sieve properties, Van der Waals forces, surface tension of the solution

1. Introduction

The study of the processes occurring at the phase interface attracts many researchers from all over the world, and they have enormous practical and theoretical importance. A detailed description of the processes occurring at the phase interface is given in [1].

Considering these processes can be argued, the issues of adsorption of gas on adsorbents have been studied quite deeply and have an extensive theoretical and experimental basis.

But the behavior of the adsorbed liquid on the surface of solid zeolite adsorbent is very difficult to describe and the explanation is very simple - the internal structure of the liquid is much more complex than the internal structure of gases and crystals. Comparing gas and liquid, it can be asserted that the density of the liquid is many times greater than the density of the gas. Considering and comparing the molecular level, the distance between molecules in liquids is

so small that the properties of the liquid are largely determined by the intrinsic volume of the molecules and by the mutual attraction between them, while in gases under ordinary conditions the influence of these factors is negligible and can be neglected. Small distances in fluid molecules impose certain limitations on the mathematical models being developed and also impose serious limitations that require taking into account the polar properties and geometric parameters of the molecules [2].

The properties of polar liquids depend on the interaction of the molecule with the molecule, but also on the interaction between individual parts of different molecules [2].

The first attempts to create a theory of fluid and to develop a mathematical model for analyzing the behavior of liquid molecules were based on a comparison of the liquid with mathematical models of the behavior of molecules in gas and did not yield any practical results, since they did not reflect the complexity of the interaction between molecules in the liquid [2].

The verification and application of new methods for analyzing the internal structure of liquids made it possible to establish the polarity of the molecules studied and the dielectric properties. And the use of nuclear magnetic resonance has led to the development of models for describing the behavior of molecules in a liquid [2].

It is established that the molecules of the liquid have a polarity, in addition, the attraction between them, inherent to nonpolar molecules, which manifests itself in a weak interaction between different parts carrying an electric charge. The total effect of mutual attraction of molecules is often described as the internal pressure of a liquid. For liquids other than electrolytes or weak electrolytes, the internal pressure varies from 3000 to 6000 bar under standard conditions [2]. At strong electrolytes, it can reach 10,000 bar. A large internal pressure, which is inherent in electrolyte liquids, characterizes the rest of their properties, such as considerable absorption of heat during evaporation and low compressibility [2].

2. Drying of liquid media

The moisture content of organic liquids significantly changes the properties of the materials. In this regard, their dehydration is of great importance.

Dewatering freon refrigeration oils: The reliability and durability of airtight refrigeration machines largely depends on the purity of the refrigerants and lubricating oils. Up to 80% of the contaminants generated in freon refrigerating machines, which cause corrosion of the system, and ultimately, the combustion of the built-in electric motors is associated with the presence of moisture [3].

When drying oil with zeolites without a binder (NaA), the degree of drying, the time of the protective effect of the layer and the dynamic activity increase significantly [3].

Dehydration of transformer oil: Methods of dehydrating transformer oil with zeolites and oil degassing are developed on the basis of mass transfer processes. In the adsorption method, contacting the oil with zeolites is carried out at ordinary temperatures and, as a result, does

not cause oxidative processes that occur during heating. The adsorption process is widely used for the recovery of waste transformer oils, for decreasing the dielectric losses of fresh transformer oils, for drying oils with zeolites, in filters for continuous regeneration of transformer oil, and so on [3].

Removal of radionuclides from liquid wastes of nuclear power plants: Synthesis of ceramic matrices by the method of sorption of radionuclides on zeolites and their subsequent conversion to feldspar allows using radionuclides to remove radionuclides from liquid wastes using a simple process scheme [3]. This method is based on the ability of synthetic zeolites with high selectivity to react with respect to Sr and Cs. Zeolites are completely iso-chemical to feldspars; moreover, the ion-exchange sorption process makes it possible to obtain zeolites of a given composition, and this process is relatively easy to control. Ion exchange on zeolites is technologically well developed and is widely used in the industry for purification of liquid waste [3].

2.1. The mechanism of the penetration of atoms and molecules through the windows of molecular sieves

The mechanism of the passage of molecules through the windows connecting the cavities of zeolites is complex because here are faced with the peculiarities of the forces of attraction and repulsion between individual molecules and atoms, as well as the structure of molecules and the structure of zeolites [4].

Numerous studies have shown that molecular sieves with a small size of the connecting windows (e.g., 5 Å) adsorb paraffin hydrocarbons of normal structure, but they do not adsorb the isomers of these hydrocarbons, since they have a branched structure and cannot pass through these channels. **Figure 1** shows that isooctane cannot pass through a window of molecular sieves with a diameter of 4.9 Å, while normal octane passes freely [4].

Adsorption of molecules, whose size is close to the diameter of the entrance windows of the zeolite, proceeds with the expenditure of additional energy. The possibility of deforming molecules containing two or more atoms within a small range makes it possible to adsorb molecules even within a larger critical diameter, through the window size [4].

Figure 1. The separation of normal octane (a) and isooctane (b) into calcium containing zeolite.

For example, through the windows NaA penetrates into the internal structure of ethane molecules having a critical diameter of 4 Å; penetration facilitates the thermal pulsation of the crystallite lattice. However, at some temperature characteristic of the sorbed material, the kinetic energy reserve of the molecule becomes insufficient to overcome the energy barrier; below this temperature, the substance is not sorbed by the zeolite of this type [4].

In **Figure 2** (according to R. Barreru) are curves showing how the adsorption of some gases changes with NaA-type zeolites, but as the temperature decreases. At 0°C, oxygen is only slightly adsorbed by zeolites, but at a temperature of liquid nitrogen, that is, at -196° C, approximately 12 molecules of oxygen are adsorbed in each cavity. For 1 g of zeolite, this will be about 130 cm³ of oxygen (when reduced to normal conditions). Thus, there is a process of adsorption of oxygen, on a zeolite accompanied by an increase in the adsorption capacity in oxygen with a decrease in temperature [4].

However, the adsorption of other gases (nitrogen and argon) occurs differently. As the temperature decreases, initially the adsorption of these gases increases, goes also as oxygen, but then, having reached a certain maximum, sharply decreases. The maximum adsorption of nitrogen is achieved at -120°C and argon at -150°C. At very low temperatures (-190°C and below), the adsorption of nitrogen and argon becomes quite insignificant compared to its maximum value [4].

Figure 2. Adsorption of some gases by zeolites at low temperatures. (X)—number of molecules in each cavity; (Y)—temperature in degrees.

Even at a temperature of -196°C , the windows between the cavities do not contract so much that the oxygen molecules cannot shine through them. At the same time, larger molecules of nitrogen and argon do not pass through the windows at very low temperatures, as a result of a decrease in their cross section.

Studies have shown that even relatively small changes in the cross section of the windows connecting the surfaces lead to significant changes in the nature of the adsorption of the individual components. Both shabasite- and CaA-type screens adsorb normal hydrocarbons, but they do not adsorb isomers of hydrocarbons having a branched structure that cannot pass through the windows of these zeolites [4]. However, in crystals of both types, a certain difference in adsorption is observed, and shabasite adsorbs different normal hydrocarbons unequally [4]. The greater the molecular weight of the hydrocarbon, the slower it adsorbs the shabasite. For example, u-heptane is not adsorbed insignificantly [4]. At the same time, synthetic molecular sieves of the CaA type adsorb even a normal hydrocarbon such as tetradecane ($\text{n-C}_{14}\text{H}_{30}$), the hydrocarbon chain of which is twice as long as n-heptane [4].

Different types of natural and synthetic zeolites have windows of unequal dimensions [4]. The penetration of molecules through these windows depends on the properties of those ions that are located at the edges of the window. A cation that compensates for the charges of the Si—O or Al—O complex is often located at the edge of the inlet (window) and prevents the penetration of molecules whose dimensions exceed the critical diameter, that is, the diameter that allows the molecule to penetrate through the narrowed window due to the presence of the cation [4].

2.2. Effect of water on zeolites

The addition of water to the dehydrated zeolites results in a pronounced change in the electrical conductivity. With an increase in the water content at a temperature of 25°C , the electrical conductivity of zeolite X increases by a factor of 10^4 . In the case of type A zeolite, the electrical conductivity increases nonlinearly, which indicates preferential hydration of cations of the same type.

In the case of type A zeolite, electrical conductivity increases with hydration until the water content is about five molecules per unit cell. This is equivalent to the hydration of four mobile sodium ions, in the vicinity of the eight-membered oxygen rings forming the entrance windows. Apparently, these sites have the highest adsorption energy. Complexes of water-sodium ions, localized in eight-membered rings, very effectively block the entrances and prevent the penetration of other molecules there.

Thus, it can be concluded that the circumstances confirm the results of the determination of physical adsorption, showing that in the presence of even traces of water adsorption of gases of the oxygen type does not occur.

Hydration of water molecules is accompanied by the formation of an unstable bond with sodium ions, and the localization of ions, and there is also an insignificant increase in the electrical conductivity of the sample. After the number of water molecules in each unit cell

exceeds 16, H₂O molecules occupy places with the lowest adsorption energy, forming hydrogen bonds with the anionic surface of the zeolite. As the crystals are saturated with water, the electrical conductivity of the zeolites increases; therefore, the system of channels is filled with water molecules. Some of the sodium ions remain sufficiently free to chaotically move through the channels of the zeolites. These conclusions are in agreement with the data of IR (adsorption of water) and NMR spectra.

2.3. Hypothetical properties of zeolites

The first works of prediction of skeletons were carried out in the 1960s of the past century [5]. Most of these pioneering studies were performed manually. The development of computer technology and new algorithms allowed the generation of millions of hypothetical structures of zeolites [6, 7]. At present, there are two main directions for forecasting zeolite frames. One of the directions is based on the creation of hypothetical zeolites with given structural features. These hypothetical scaffolds are of great importance for functionally oriented synthesis [8, 9]. Another way of predicting zeolite frames is to create as many hypothetical structures as possible and enumerate all possible three-dimensional grids under certain topological and geometric constraints [10, 11]. Thus, in [12, 13], in order to enumerate all possible four-connected grids with a given number of unique T-atoms for all spatial groups, generation of hypothetical structures was carried out, consisting of the following basic procedures:

- Crystallographically unique T-atoms were successively placed in different positions (private and general) of the unit cell and by means of symmetry operations were generated on the whole cell.
- Of all the possible distributions of T-atoms in the cell, those that allow tetrahedral coordination of atoms are selected.
- When the parameters of the unit cell were varied, optimization was performed to obtain acceptable values for the distances T–T and the angles T–T–T. At the last step, oxygen atoms were added between the bound T atoms, and the whole cell was optimized. As a result, several million hypothetical four-connected zeolite frameworks were obtained with a number of unique T-atoms ≤ 7 , which are now presented in an online database [12, 13].

2.4. Zeolite Molecular Sieve

Zeolites are molecular sieves [4, 14]. Their wide application that they can be used for the separation of substances, not only on the basis of selectivity of adsorption, but also on the basis of the difference in size and shape of the molecules to be absorbed. In order to penetrate the adsorption cavity, the critical diameter of the adsorbate molecules must be smaller than the size of the entrance window [15].

The main factor determining the molecular sieve properties is the size of the entrance windows of zeolites, which depends on the location of the oxygen rings of the zeolite and on the number of oxygen atoms in the ring. The size of the input window is also affected by the size

of the cation entering the zeolite. Cations located close to the window block the entrance for molecules. For example, in cation exchange, in which two sodium cations are replaced by a single calcium cation, the input window expands; As a result, the Na zeolite has an inlet window size of 4Å, and the CaA zeolite has a size of 5Å [15]. A similar exchange in a zeolite of type X leads to a certain narrowing of the window. Considering the properties of the KA zeolite, it can be explained that, at ordinary temperatures, this kind of zeolite sorbs water very well. This property has prevented its use for the drying of unstable substances prone to polymerization reactions.

If we consider the property of NaA zeolite, which is capable of sorbing most of the components of industrial gases, the critical size of the following molecules does not exceed 4Å: hydrogen sulfide, carbon disulfide, carbon dioxide, ammonia, lower diene and acetylene hydrocarbons, ethane, ethylene, propylene, organic compounds with one methyl group in molecule, as well as methane, neon, argon, krypton, xenon, oxygen, nitrogen and carbon monoxide [15]. The latter group of substances is absorbed in considerable quantities only at low temperatures. Propane and organic compounds with more than three carbon atoms in the molecule are not adsorbed by the zeolite and thus do not suppress the adsorption of the above impurities during drying and purification.

CaA zeolites adsorb hydrocarbons and alcohols only of a normal structure, and therefore, it is widely used in the processes of separation of multicomponent organic substances on a molecular sieve basis. Moreover, zeolite CaA is absorbed by methyl and ethyl mercaptans, organic compounds with the number of carbon atoms in molecule 2 (ethyl alcohol, ethylamine), diborane, and so on. Among the general-purpose zeolites of CaA type is increased resistance in a weakly acid medium, and therefore, it is used in desulfurization processes and decarbonization of gases.

Zeolites of type X have rather wide entrance windows and adsorb the vast majority of the components of complex mixtures: all types of hydrocarbons are organic sulfur, nitrogen and oxygen compounds (mercaptans, thiophene, furan, quinoline, pyridine, dioxane, etc.), halogenated hydrocarbons (chloroform, carbon tetrachloride and freons), pentaborane and decaborane [15]. The use of zeolites of CaX and NaX is based on the selectivity of adsorption and not on molecular sieve properties. With the complete replacement of the sodium cation for calcium, the zeolite of CaX, unlike the NaX zeolite, does not adsorb aromatic hydrocarbons or their derivatives with branched radicals, e.g., 1, 3, 5β-triethylbenzene and metadichlorobenzene. This method is based on the method for identifying the zeolites of these two types and establishing the completeness of the ion exchange in the preparation of the zeolite of CaX.

In the case when the critical diameter of the molecule is close to the diameter of the input window, the adsorption process occurs with a high activation energy and the ad-molecule must have a certain kinetic energy reserve to overcome the energy barrier. The kinetic energy of molecules rises with increasing temperature [15]. At the same time, an increase in temperature leads to an increase in the thermal pulsation of the zeolite lattice, which facilitates the penetration of the molecule into the adsorption cavity. Thus, by changing the temperature regime, it is possible to reach a point at which the adsorbent molecules begin to be absorbed by the zeolite.

Localization of cations in the zeolite structure: The localization of cations in the structure depends on the degree of hydration of the zeolites. Dehydration promotes the migration of cations in its structure, and it is necessary to take into account the degree of hydration of the zeolite under given conditions. In addition, protons from 100°C also show increased mobility. The location of the cation is determined not only by the degree of hydration of the zeolite, but also by the nature of the reacting substances. Thus, it was shown that in zeolites of type Y a significant number of Ni^{2+} and Cu^{2+} ions again move from small cavities to large ones when the latter are filled with olefins, ammonia, pyridine or NO molecules [16].

In NaA zeolite, the possible sites for cation localization are four-, six- and eight-membered rings and large cavities. Cations in the eight-membered rings react to the pore size due to the partial blocking of the entrance windows of the cavities [16]. In the faujasite structure, the cations are localized apparently at the centers of hexagonal prisms and on six- and four-membered rings.

The catalytic properties of zeolites, which are studied using X-ray diffraction analysis, should be carefully considered; in fact, the localization of cations largely depends on the conditions for pretreatment of the zeolite: the heating rate and the final temperature of the zeolite, the concentrations and the parameters for calcinations, the thickness of the layer and the possibility of reducing the cations by hydrocarbons, and also from the possibility of separation from the vacuum lubricant used in installation.

As a rule, when analyzing the cation distribution in faujasite, the following factors are taken into account [16]:

1. the need for optimal coordination; in hexagonal prisms, cations are easily coordinated with six skeleton oxygen atoms, whereas in the sodalite cavities tetrahedral coordination with three skeleton oxygen atoms and one residual water molecule is possible;
2. the difficulty of local charge compensation with the help of multiply charged ions;
3. the need to minimize the electrostatic energy of the system (direct repulsion of the cation-cation should be excluded);
4. stabilization by a crystalline field or a field of ligands;
5. covalence and the existence of directed bonds.

2.5. Adsorption properties of zeolites

Considering the term adsorption can be understood this term as the ability of solids to absorb certain substances. This ability is closely related to the special properties of the surface of solids. Molecules of a gaseous or liquid substance are in contact with a solid, adsorbed by the surface of solids. The larger the surface of a solid, the more the amount of gas or liquid a given body can hold [4].

If the adsorbed substance is located for a long time on the surface of the adsorbent, the process of diffusion of adsorbed molecules inside [4] of the solid begins. Molecules of gaseous and

liquid substances adsorbed on the surface of a solid. They have a certain mobility, due to which they gradually penetrate into the solid body.

At low pressures, adsorption increases in proportion to the increase in pressure. However, as the pressure rises, the linear relationship is broken; the amount of adsorbed gas decreases, and then, at a certain pressure, saturation appears; with further increase, the pressure of adsorption of substances does not increase [4].

In a number of cases, the relationship between the gas pressure and the amount of gas absorbed by the adsorbent is more complex; after reaching a certain pressure, the amount of adsorbed gas begins to increase sharply. It was found that the nature of this dependence is related to the shape and size of the adsorbent pores [4].

In the adsorbent pores, at a certain relative pressure, the vapor becomes a liquid state and the entire internal structure begins to be filled with condensing vapor, as a result of which the amount of absorbed substance sharply increases. This phenomenon is called capillary condensation. In the fine pores of molecular sieves, capillary condensation does not occur; it can be noted only in relatively large pores formed by a binder during granulation—in a secondary porous structure [4].

Theories were advanced to explain the features of adsorption processes, and equations describing the dependence of the amount of adsorbed matter on pressure, temperature, and other conditions were derived.

The theory developed by Langmuir proceeds from the concept of the formation of a monomolecular layer of an adsorbed substance due to the action of active sites of the adsorbent.

In the potential theory advanced by Polanyi, it is assumed that the scope of the attractive forces during adsorption extends not only to the nanomolecular layer of matter.

Proceeding from all of the above, the main ways to regulate the selective adsorption capacity of zeolites are as follows.

1. Change in composition in the process of crystallization. From the same starting materials, it is possible to obtain aluminosilicate porous crystals having different properties. For example, type A zeolite is formed from mixtures rich in alkalis and poor in silica, and type Y zeolite crystallizes in the region with the lowest alkalinity of the medium and the highest concentration of silica [17].
2. Method of ion exchange. Ionic exchange can be regulated by molecular sieve properties, especially type A. Knowing the dimensions of the adsorbed molecules and zeolite windows, it is possible to select a particular cation exchange form of the zeolite to separate any mixture of gases or dissolved gases. For example, a zeolite, a spacecraft with a window size of about 3 Å, adsorbs water well, but water does not adsorb molecules of methanol, carbon dioxide, whose critical molecular diameter is greater than 3 Å. Zeolite NaA in which the window size is 4 Å adsorbs methanol and carbon dioxide and does not adsorb the molecules of propane, hexane and other molecules with a critical diameter greater than 4 Å. On a CaX zeolite with a window size of 8 Å, 1,3,5-triethylbenzene molecules are not adsorbed, and on NaX zeolite (the size of windows 9 Å) they are well adsorbed [17].

Zeolites can manifest themselves as ions in many processes. For example, sodium in zeolite type X cannot be exchanged for alkyl ammonium cations because of the large size of the latter. Cation sieve effects in zeolites can also be caused by the fact that due to too large a size the cation cannot penetrate into small channels and cavities in the zeolite framework, or exchange cations during the synthesis of some zeolites are localized in inaccessible areas and therefore not are replaced [17].

Adsorption on the surface of zeolite of polar substances, around the entrance windows, prevents the diffusion of adsorbate molecules, and prevents their movement. Thus, for example, the pre-sorption of small amounts of water vapor on zeolite type A sharply reduces the adsorption of oxygen. Effective window diameters can be adjusted to form organometallic complexes. Thus, when pyridine is treated with a copper form of zeolite X, a very strong pyridine cation complex is formed. The adsorption of molecules of gases and vapors on such a zeolite indicates a significant decrease in pore sizes due to their blocking by organometallic complexes [17].

A special place among the cation-substituted zeolites is occupied by hydrogen, or decationized, forms of zeolites. Replacement of cations of zeolite with hydrogen is one of the ways of modifying porous crystals. The hydrogen form of zeolites, unlike other forms, cannot be obtained by simple treatment of the zeolite with acids, since the latter destroy the crystal lattice, especially low-silica zeolites. Therefore, in the beginning, sodium ions are replaced by ammonium ions, then the latter is thermally decomposed, ammonia is released and a proton is formed, which ensures the neutrality of the zeolite lattice [17].

One of the methods for modifying zeolites is dealumination. Treatment of zeolite with acids leads to the dissolution of tetrahedral aluminum in the lattice. As a result, the adsorption capacity of the zeolite increases. Dealumination can also be carried out by treating the zeolite with substances that form complex compounds with aluminum ions or by treating the zeolite layer with water vapor at elevated temperatures [18]. Dealumination allows, within certain limits, to vary the ratio of silicon and aluminum-oxygen tetrahedra in the zeolite without changing its crystal lattice.

Selective adsorption on zeolites is also possible when the molecules of all components of the mixture are sufficiently small and freely penetrate into the adsorption space. Other things being equal, the exchange cations are adsorption centers and determine the specificity of the interaction during adsorption on the zeolites of molecules of different structure and electronic structure [18]. By changing the nature and size of the exchange cation, it is possible to enhance or weaken the contribution of a specific interaction to the adsorption energy. In addition to interacting with the positive charge of cations, the adsorbate molecule undergoes strong dispersion effects from other atoms forming the walls of the zeolite channels. One of the important issues of adsorption interaction on zeolites is the elucidation of the nature of active centers [18].

2.6. A mathematical model for determining the total adsorption of solutions on zeolites

Considering the process of adsorption from solutions should be considered as a process of concentration on the surface of one of the two adsorbed components. Therefore, to determine

the adsorption energy of solutions, we use the data on the surface tension of the pure components and try to obtain the adsorption through Gibbs energy.

Considering the fundamental Gibbs law, we get

$$-d\sigma = G_1 d\mu_1 + G_2 d\mu_2 \quad (1)$$

where G_1 and G_2 are the values of the Gibbs adsorption of components; μ_1 and μ_2 are the chemical potential of the components in order to relate Gibbs adsorption to the concentration of the component; it is necessary to use the Gibbs-Duhem Eq. [19]

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \quad (2)$$

where x_1 and x_2 are the mole fraction of the components.

Then,

$$\mu_1 = -\frac{x_2}{x_1} d\mu_2 \quad (3)$$

We substitute it into the Gibbs Eq. (3) and obtain

$$-d\sigma = \left(G_2 - G_1 \frac{x_2}{x_1} \right) d\mu_2 \quad (4)$$

Surface properties of solutions are considered from the surface properties of pure liquids and strongly depend on the composition of the surface layer [20]. When a substance having a lower surface tension than a pure solvent dissolves, the surface tension of the solution decreases spontaneously, since the free energy of the system decreases. The concentration of solute in the surface layer as compared to its concentration in the solution volume increases [20]. Substances that increase the surface tension of the solution, on the contrary, are contained in the surface layer in a lower concentration than those in the volume [20].

Often substances that increase the surface tension of the solvent themselves have a higher surface tension in their pure form, while lowering substances have a lower surface tension than the solvent. A large surface tension means greater energy unsaturation of molecules on the surface [20]. Such molecules tend to leave the surface, since to reduce free surface energy it is more advantageous to have molecules with low energy unsaturation. Naturally, the complete separation of molecules is impeded by the loss of entropy of solution formation [20]. As a result of the action of these two factors, a composition change occurs on the surface of the solution as compared with the volume, that is, adsorption occurs [21]. For all liquid organic substances, the surface tension is less than the surface tension of water. Assuming that the total number of moles before and after adsorption remains unchanged, we find that when one component is adsorbed, the amount of the other is increased evenly. Then, $G_1 = G_2$, $x_2 + x_1 = 1$. From this, it turns out:

$$G_2 = (1 - x_2) \frac{d\sigma}{d\mu_2} \quad (5)$$

and replacing μ_2 by c_2 , we obtain an equation similar to the Gibbs adsorption equation for dilute solutions

$$G_2 = (1 - x_2) \frac{c_2}{RT} \frac{d\sigma}{dc_2} \quad (6)$$

Thus, the most important feature of the Gibbs method is that it allows us to give some general characteristic of the region of inhomogeneity without knowing the true course of the concentration profile.

To solve Eq. (6), it is necessary to find the value of the surface tension for a binary solution.

Determination of the surface tension of a binary solution is

$$\sigma = \sigma_0 + 0.049 \cdot \left(1 - \frac{c_2}{c_1}\right) \quad (7)$$

where σ_0 is the surface tension of water; c_1 is the initial concentration of the solution, % vol.; c_2 is the final concentration of the solution, % vol.

Since Gibbs adsorption does not allow comparison of the results with the results of the experiment, it is necessary to use the equation to determine the total adsorption. Let us single out that to determine the total adsorption (absolute adsorption), it is necessary to relate Gibbs adsorption to the experimental results [21–24].

$$a = G_2 + W \cdot \rho \quad (8)$$

where W is the volume of the space in which adsorption occurs, cm^3/g ; a is the complete adsorption of g/g ; ρ is the density of the equilibrium phase, g/cm^3 .

Then,

$$a = (1 - x_2) \frac{c_2}{RT} \frac{d\left[\sigma_0 + 0.049 \cdot \left(1 - \frac{c_2}{c_1}\right)\right]}{dc_2} + W \cdot \rho \quad (9)$$

Thus, Gibbs adsorption does not reflect the properties of zeolite adsorbents; therefore, it is necessary to combine the formulas (6)–(8) into a single equation for the theoretical calculation of the total adsorption of binary solutions on zeolites. With the application of the method of complete content, from the concept of the region of inhomogeneity at the interphase interface as a separate real phase of finite volume [22–24].

3. Experimental part

As a result of experimental research in the laboratory, the following hydrometer Hydrometer AHON-1 (measuring range $700\text{--}1840 \text{ kg/m}^3$), laboratory scales Leki 5002, calipers digital 31C628 (error) and SORBTOMETR-M were used.

Adsorbent	Diameter of grain, mm	a , total adsorption, g/g	W , the volume of the space in which adsorption takes place, cm ³ /g
Zeolite CaA	3	0.26	0.23
Zeolite CaA		0.191	0.17
Zeolite NaA		0.245	0.2
Zeolite NaX		0.304	0.292
Zeolite KaA		0.197	0.1912

Table 1. Characteristics of zeolite adsorbents of grades A, X [24, 25].

Name	c_1 —initial concentration of water, % vol.	c_2 —final concentration of water solution, % vol.	Density of the solution, g/m ³	x_2 —mole fraction of components	Temperature T , K
C ₂ H ₅ OH (65%)	35	25	0.8795	0.58	293
CH ₃ OH (75%)	25	15	0.8616	0.38	293
C ₆ H ₆ (60)	40	30	0.836	0.76	293

Table 2. Characteristics of the investigated organic substances.

The following characteristics of the investigated adsorbents are established (**Table 1**). The volume of the solution is 200 ml, and the mass of adsorbent for adsorption is 100 g.

To check the theoretical relationships and compare them with the experimental data, it is necessary to analyze a number of binary solutions, such as ethanol + water, methanol + water, and benzene + water; we distinguish that in **Table 2** the characteristics of the pure components of organic solutions for theoretical calculations are listed.

For a simplified calculation, let us set the condition that adsorption in the systems under consideration occurs only for one of the components; therefore, the concentration change will be monitored by the change in the percentage of water in the solutions in question. To do this,

Adsorbent	a —total adsorption, g/g		
	C ₂ H ₅ OH + H ₂ O	CH ₃ OH + H ₂ O	C ₆ H ₆ +H ₂ O
Zeolite CaA	0.202	0.198	0.192
Zeolite CaA	0.15	0.146	0.142
Zeolite NaA	0.176	0.172	0.167
Zeolite NaX	0.257	0.252	0.244
Zeolite KaA	0.169	0.165	0.16

Table 3. Calculated values of total adsorption.

when testing the mathematical model for calculating the total adsorption, we take the initial water concentration of the binary systems under consideration. The results of the calculation using formula (9) are given in **Table 3**.

4. Conclusion

The data presented show that the mathematical model developed by the author allows us to reliably estimate the total adsorption of various binary systems. When comparing theoretical values with experimental ones, it can be asserted that the values obtained fully satisfy the requirements of theoretical calculations and can be used in the design of drying apparatuses and concentrating alcoholic solutions. Let us emphasize that the accumulation of data on Gibbs adsorption will contribute to the refinement and verification of models taking into account bulk effects in adsorption solutions and will allow theoretical calculations to be carried out with high accuracy [26, 27].

Thus, the use of the approximate method of calculating absolute adsorption makes it possible to obtain more realistic information about the properties of adsorption solutions, which indicates significant structural changes in them, depending on the concentration.

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