

Adsorption properties of the diatomite carrier Chromaton N-AW modified with inorganic salts

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This paper deals with adsorption and structural properties of the Czechoslovak diatomite carrier Chromaton N-AW after its modification with inorganic salts, *i.e.* LiCl, NaCl, and KCl. It has been ascertained that the chemical modification results in a decrease in specific surface and open porosity and significantly affects the adsorption of methanol. The interpretation of adsorption measurements is based on the idea that new adsorption centres arise on the surface of the modified adsorbent.

В работе изучены адсорбционные и структурные свойства чехословацкого диатомитового носителя Chromaton N-AW после его модификации неорганическими солями LiCl, NaCl и KCl. Было обнаружено, что химическое модифицирование вызывает понижение удельной поверхности, открытой пористости и отчетливо влияет на адсорбцию метилового спирта. Объяснение адсорбционных данных исходит из представления об образовании новых адсорбционных центров на поверхности модифицированного адсорбента.

The diatomite adsorbents belong to the most used carriers in gas chromatography. Although the properties of these substances are regulated during their production [1], we frequently observe an enhanced activity of these carriers especially with respect to adsorbates of the polar type in gas chromatography. The increased adsorption activity of diatomites manifests itself by higher retention times, conspicuous asymmetry of peaks and, as for the analysis of mixtures, by decreased distribution ability. The adsorption activity may be affected by several ways, *e.g.* by washing the adsorbent with an acid, by reaction of the surface OH groups with silanes, saturation of the adsorption centres with liquid phase or by applying solid phase to the adsorbent.

The commercial preparations of the type AW, e.g. Chromaton N-AW [2] procurable in Czechoslovakia may be obtained by washing the adsorbents with acids. The silanization and application of liquid phase belong to the classical methods of treatment of adsorbents and have been described by *Ottenstein* for diatomites [3].

The modification of adsorbents with inorganic salts was for the first time used in gas chromatography by *Scott* [4]. This author pointed out the improvement of chromatographic properties of alumina by applying the NaX salts ($X = OH, Cl, Br, I$) to its surface. Later, these chemically modified carriers were used for analysis of more complicated mixtures [5, 6]. *Favre* [7] successfully tested the inorganic salts themselves as adsorbents. Recently, *Lycourghiotis* [8] studied properties of the alumina modified with lithium chloride.

The modification of the diatomite carriers by applying a solid phase has been given little attention. *Omerod* [9] applied 40 wt % of silver to Chromosorb P and wetted this adsorbent with Apiezon. The peaks of alcohols on this carrier were symmetrical but they considerably tailed if silver had not been applied.

The purpose of this study is to appreciate the physicochemical properties of the Czechoslovak diatomite carrier Chromaton N-AW modified by applying LiCl, NaCl, and KCl.

Experimental

Adsorbents

The original sample Chromaton N-AW (Lachema, Brno), fraction 0.125—0.160 mm.

The modified samples were prepared as follows: The inorganic salts (LiCl, NaCl, KCl) in the amount of 20 wt % of the overall weight of the carrier were dissolved in water. After adding Chromaton N-AW to particular solutions, the suspensions formed were thoroughly homogenized, dried and exposed to a short-term heating at 1183 K.

Adsorbates

Methanol anal. grade (Lachema, Brno) and n-hexane anal. grade (Fluka, A.G., Buchs, Switzerland) were used.

In order to characterize properties of the adsorbents, we measured their densities, specific surface, porosity and determined adsorption isotherms of the above adsorbates.

Density

Density was determined with pycnometer by using benzene as adsorbate. We measured the so-called real density [10].

Specific surface

Specific surface was estimated by the method of thermal desorption [11] using a hydrogen—nitrogen mixture as a carrier gas. Before measurements the samples of the

Table 1

Properties of adsorbents

Adsorbent	Real density 10^3 kg m^{-3}	Specific surface $10^3 \text{ m}^2 \text{ kg}^{-1}$	Porosimetric data ^a	
			Total volume of pores $10^{-3} \text{ m}^3 \text{ kg}^{-1}$	Open porosity %
Chromaton N-AW (CNAW)	1.70	1.25	1.3 ^b	—
CNAW + 20% LiCl	1.41	0.96	0.26	36.21
CNAW + 20% NaCl	1.59	1.02	0.32	49.53
CNAW + 20% KCl	1.55	1.16	0.35	55.33

a) Range of open pore measurements 2500—3.75 nm.

b) Value taken from paper [14].

adsorbents were degasified in the flow of the carrier gas for 1 h at 423 K. Chromosorb W-AW (Applied Science Laboratories, USA) was used as standard. The calculated values of specific surfaces as well as the densities are given in Table 1.

Adsorption isotherms

The measurements were carried out on a chromatograph Chrom 41. The original columns were replaced by stainless steel columns of proper construction (length 0.11 m, inside

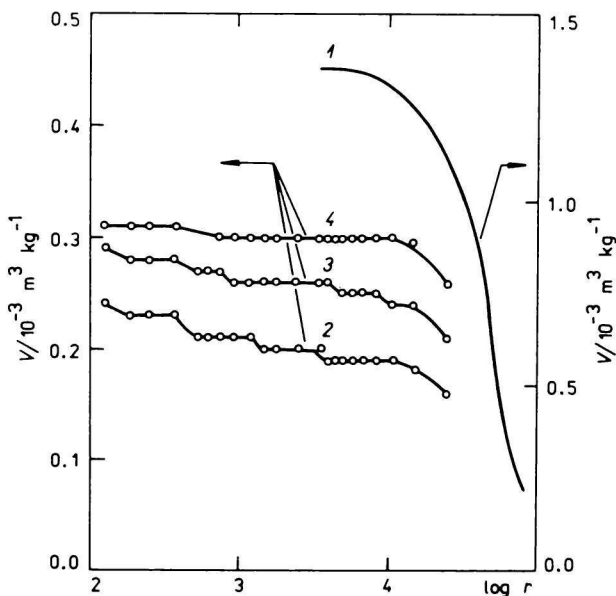


Fig. 1. Variation of V with $\log r$ for Chromaton N-AW (1) [14] and the samples modified with inorganic salts: LiCl (2), NaCl (3), and KCl (4).

diameter 0.006 m). Conditions of measurements: temperature of column 393 K, carrier gas — nitrogen (flow rate $3 \text{ dm}^3 \text{ h}^{-1}$), temperature of feed block 413 K, thermal conductivity detector (temperature 413 K, filament current 90 mA). Before measuring the adsorption isotherms, the adsorbents were processed for 1 h in the flow of the carrier gas at 473 K. Afterwards, the temperature was reduced to working temperature and the measurements were performed. The adsorbates were dosed with microsyringes of the type 701 N (Hamilton, Bonaduz, Switzerland). The adsorption isotherms $a(p)$ calculated from the elution data according to *Kiselev* [12] are represented in Figs. 1 and 2 (a — adsorbed amount of the adsorbate per unit surface, p — equilibrium pressure of the adsorbate).

Porosimetry

The porosimetric data for the modified adsorbents were obtained with a high-pressure mercury porosimeter 70 H (C. Erba, Milan) in the Institute of Experimental Metallurgy of

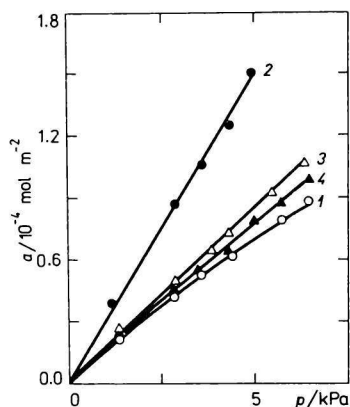


Fig. 2. Adsorption isotherms of n-hexane on Chromaton N-AW (1) and the samples modified with inorganic salts: LiCl (2), NaCl (3), and KCl (4).

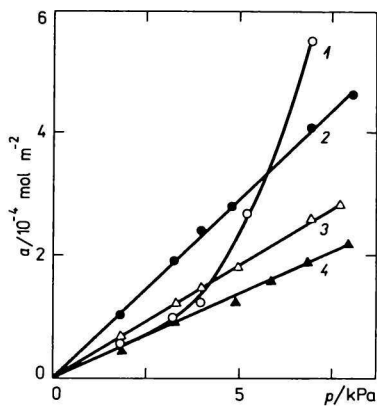


Fig. 3. Adsorption isotherms of methanol on Chromaton N-AW (1) and the samples modified with inorganic salts: LiCl (2), NaCl (3), and KCl (4).

the Slovak Academy of Sciences, Košice. The instrument works in the range 0—200 MPa and enables us to measure open pores in the range of pore radii 7500—3.75 nm. The relationship between V and $\log r$ is represented in Fig. 3. From the porosimetric curves, we are able to calculate other data [13] which are summarized in Table 1.

Results and discussion

On the basis of surface, structural, and adsorption characteristics the results obtained show the extent of the changes in properties of Chromaton N-AW after its modification with inorganic chlorides.

According to the data given by *Kalina* [15], the specific surface of Chromaton N is $1.0 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$. As to Chromaton N-AW, the washing with an acid results not only in removal of the heavy metals but also in elution of powder particles, which brings about a greater accessibility of the surface for the molecules of the adsorbate and manifests itself in an increased value of the specific surface (Table 1). The specific surface of the modified samples is smaller than that of the original sample. This decrease is likely to be due to two simultaneous effects:

1. During preparation the modified adsorbents are heated to 1173 K. This temperature is sufficient to produce chemical and structural changes in the adsorbent. *Scholz* [16] states that the chemisorbed water in the diatomites escapes at temperatures over 873 K. This escape is accompanied by a decrease in specific surface of diatomites. It is very probable that the liberation of this water (water bound by physical adsorption escapes at rather lower temperatures) is accompanied by a rearrangement of the surface OH groups into the siloxane groups as observed with pure SiO_2 [17]. *Bryzgalova* [18] points out a decrease in specific surface and porosity of diatomites E-23 and INZ-600 after their sintering at 1373 K.

2. The decrease in specific surface is also caused by choking of the pores of Chromaton N-AW with inorganic chlorides. *Gavrilova* [19] mentions a similar effect ensuing from MoS_2 brought in the pores of Chromosorb W.

Since the high-temperature heating and chemical modification of Chromaton N-AW are simultaneous, these effects cannot be differentiated from each other.

As obvious from the data in Table 1, the real density of the modified samples is lower than that of the original sample. This density is a measure of proper weight of the adsorbent (without pores) and is related to the specific weights of individual adsorbents (specific weight of the skeleton of Chromaton N-AW is higher than the specific weights of chlorides).

The porosimetric data indicate changes in structure of the adsorbents. A considerable decrease in total volume of pores of the modified samples is to be observed and the relationship between V and $\log r$ (V = total volume of pores, r = radius of pores) indicates a geometrical inhomogeneity of the adsorbents with a broad distribution of pores of various size and a frequent occurrence of micropores. A decrease in total volume of the pores is related to a decrease in specific surface of the adsorbents.

The interaction between adsorbate and adsorbent is affected by many factors among which the chemical composition of surface and geometrical structure of the adsorbent and the properties of the adsorbate are the most important. In order to estimate influence of the properties of the adsorbate, we studied the adsorption isotherms of n-hexane and methanol on particular adsorbents (Figs. 2 and 3). These adsorbates differ from each other by different mechanism of the interaction with surface. n-Hexane is adsorbed by the weak van der Waals forces while

methanol forms hydrogen bonds with the OH groups of diatomites [16]. The adsorption isotherms of n-hexane (Fig. 2) show analogous character and the adsorption on Chromaton N-AW is the poorest. The form of the isotherms was also reflected in the forms of chromatographic peaks which were symmetrical. A more substantial difference appears in the adsorption of methanol (Fig. 3) because the isotherm on the nonmodified adsorbent (curve 1) is convex against the axis of pressure. The form of the isotherm is characteristic of the adsorption of polar substances. First of all, the interaction between adsorbate and adsorbent is operating, but it does not stop after filling the surface because it is succeeded by the adsorbate—adsorbate adsorption due to the ability of the methanol molecules to form hydrogen bonds. The chemical modification results in the linear progress of adsorption isotherms (curves 2—4). In comparison with Chromaton N-AW, the modified adsorbents exhibited not only the decrease in specific surface already discussed but also a change in quality of the adsorption centres. By applying chlorides, the most active centres were screened and the overall surface heterogeneity was reduced. That is most distinctly obvious for the adsorption of methanol the interaction of which with the surface of diatomite is more sensitive to the presence or absence of the OH groups in comparison with n-hexane which is adsorbed only by dispersion forces. Besides, various secondary adsorption centres which occur in the skeleton of diatomites owing to the presence of impurities mostly of the oxide type are also screened by this modification. The modification of carrier by the effect of inorganic salts changes the surface quality and thus the adsorption mechanism. It may be expected that the chemical properties of salt crystals, especially dimensions of cations, as well as structural defects play an important role. We suppose that the ability of cation to interact with the adsorbate molecules determines the extent of adsorption on the modified adsorbents. This ability is related to the size of the cation in the structure. The concentration of the effective charge of cations increases in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+$, which is in conformity with the order of adsorption on the modified Chromaton N-AW. *Nejmark* [20] presents equal order for the adsorption of polar substances on the Li^+ -, Na^+ -, and K^+ -zeolites and refers it to the formation of new adsorption centres on the surface of the modified zeolites.

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