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CHARACTERIZATION OF MODIFIED ALUMINA AS AN ADSORBENT FOR GAS-SOLID CHROMATOGRAPHY

MODIFICATION WITH DIPOTASSIUM HYDROGEN PHOSPHATE

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SUMMARY

The change in surface properties of modified alumina adsorbents for gas-solid chromatography (GSC) has been studied by coating alumina with dipotassium hydrogen phosphate and heating before and/or after coating. The surface properties were significantly influenced by some thermally induced changes, such as sintering, dehydration and crystallization due to a phase transition of alumina, mainly as a result of the pre-heating treatment and also of the pyrolysis of the salt and recrystallization of its product after fusion in the post-heating treatment. A dependence of solute retention volume on the temperature of heat treatment could be interpreted in terms of changes of the surface properties caused by successive coverage of the alumina surface with a monolayer, a double layer and finally a crystalline layer of the salt. The same reasoning could be applied the dependence of solute retention volume upon salt loading. The total weight of free alumina packed into the column was found to be an important parameter for describing the characteristics of the GSC column.

INTRODUCTION

Analytical applications of gas-solid chromatography (GSC) have been considerably restricted because of the less than quantitative response due to asymmetric peaks and irreversible adsorption. Such phenomena can be excluded by adjusting the

surface properties of the adsorbent used. A salt-modified adsorbent, developed originally by Phillips and Scott¹, has often been investigated as a simple and effective method for controlling surface properties of adsorbents for GSC.

We have reported that some C₅–C₈ aliphatic and aromatic hydrocarbons and their halogeno derivatives can be separated by GSC on alumina adsorbents modified with the following reagents: alkali metal fluorides², alkali metal chlorides³ and alkali metal phosphates⁴. Such modified alumina adsorbents showed class II characteristics according to Kiselev's classification⁵, *i.e.*, adsorbents bearing localized positive charges as active sites for adsorption. Their surface properties were dependent on the nature of the inorganic salt coated as a modifier, the salt loading and the temperature of pre-heating and post-heating treatments. In a previous paper⁶, we reported that the dependences on salt loading of the retention volume of each solute and of the specific surface area of the modified alumina adsorbent could be interpreted on the basis of possible modes of distributions of the salt, a monolayer and a crystalline layer, on the alumina surface.

This paper is concerned with the modification of the surface properties of alumina with dipotassium hydrogen phosphate, and constitutes an extension of our previous studies with alkali metal phosphates^{4,7}. Our attention was focused on the influences of both heat treatments on the surface properties of the original alumina and the salt-coated alumina, and the dependence of the surface properties of the modified alumina adsorbents on salt loading.

EXPERIMENTAL

Activated alumina beads, Neobead MS · C (60–80 mesh) (Mizusawa Industrial Chemicals, Tokyo, Japan), were used for preparation of salt-modified alumina adsorbents, with extra pure reagent grade dipotassium hydrogen phosphate as a modifier. Before coating, the activated alumina was pre-heated for 2 h at a temperature between 180 and 1100°C. Fifteen grams of the pre-heated alumina were then added a solution containing 0.75–7.5 g of dipotassium hydrogen phosphate in 30 cm³ of distilled water. The mixture was evaporated to dryness on a water-bath with occasional stirring. For comparison, an adsorbent with zero salt loading was prepared in the same way but using only distilled water instead of the salt solution. The salt-coated alumina were dried at 120°C for 3 h before use and post-heated at 800–1200°C for 2 h. The modified alumina adsorbent was packed into a stainless-steel column (100 × 0.3 cm I.D.) and the column was pre-conditioned for 3–4 h at 180°C in a helium gas stream before injection of solute.

A Hitachi K 23 gas chromatograph equipped with a thermal conductivity detector and a Hitachi QPD 33 recorder was used for gas chromatography. Helium gas was used as a carrier gas at a flow-rate of 40 cm³ min⁻¹. A 0.2-mm³ dose of each solute was injected into the column with a Terumo MST-10 microsyringe. The column temperature was 180°C for benzene, toluene, ethylbenzene, *o*-, *m*- and *p*-xylenes, and 80°C for *n*-pentane, cyclohexane and *n*-hexane.

The procedure described previously² was used for measurements of solute retention volumes and their corrections, and for determination of the specific surface area of the modified alumina adsorbent.

RESULTS AND DISCUSSION

The effects of both heat treatments on solute retention volume were first examined on salt-free alumina. The curves in Fig. 1 are very similar to ones obtained previously on modified alumina adsorbent coated with tripotassium phosphate. On alumina post-heated below the pre-heating temperature, a constant retention volume is obtained regardless of the post-heating temperature. This constant value decreased with increasing pre-heating temperature. The retention volume decreased with increasing post-heating temperature beyond the pre-heating one. This is similar to the monotonous decrease in water content of γ -alumina with increasing heating temperature reported independently by Bather and Gray⁸ and Zamora and Cordoba⁹. Dehydration of alumina particles can be regarded as one factor in the deactivation of their surface by heat treatment.

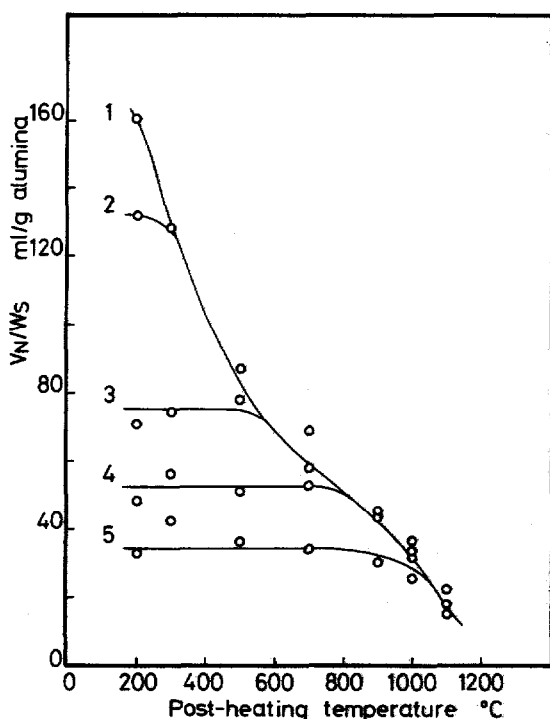


Fig. 1. Effects of heat treatments on the retention volume of toluene on salt-free alumina. Pre-heating temperature: 1, without pre-heating; 2, 300°C; 3, 500°C; 4, 700°C; 5, 900°C. V_N = net retention volume; W_s = weight of salt-free alumina packed into the column.

Fig. 2 shows some chromatograms of a mixture of benzene, toluene, ethylbenzene, *o*-, *m*- and *p*-xylenes obtained by GSC on the modified alumina adsorbent pre-heated at different temperatures and coated with 10% (w/w) dipotassium hydrogen phosphate. On the modified alumina adsorbent without pre-heating treatment, an asymmetric peak was observed with a long retention time. With increasing pre-heating temperature, the retention time and peak width of each solute peak were

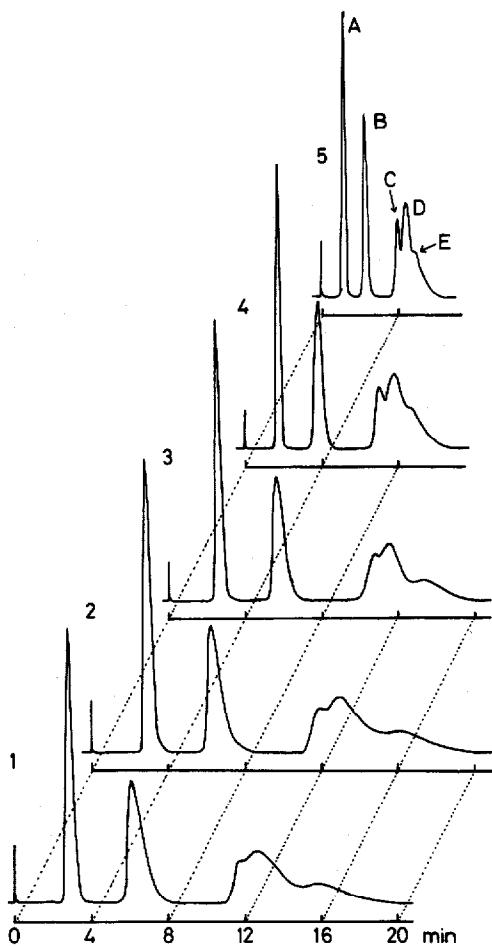


Fig. 2. Chromatograms of an aromatic hydrocarbon mixture obtained by GSC on modified alumina adsorbents pre-heated at various temperatures and coated with 10% (w/w) K_2HPO_4 but without post-heating treatment. Pre-heating temperature: 1, without pre-heating; 2, 500°C; 3, 700°C; 4, 900°C; 5, 1000°C. Solutes: A = benzene; B = toluene; C = ethylbenzene; D = *m*- and *p*-xylenes; E = *o*-xylene.

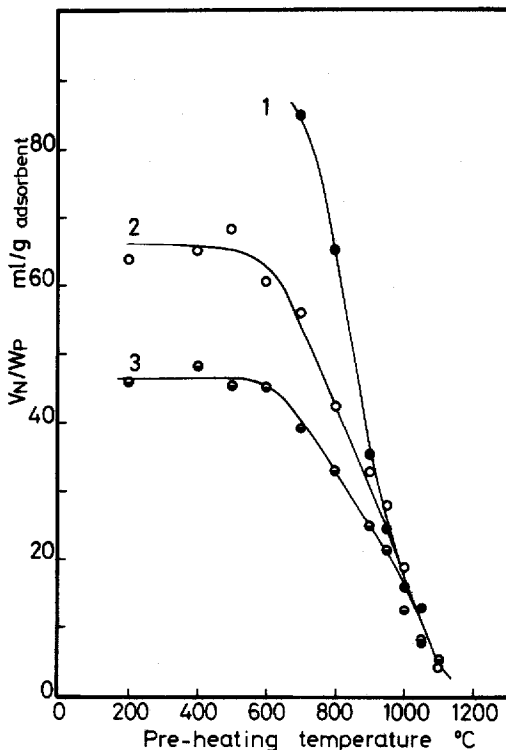


Fig. 3. Effect of pre-heating temperature on retention volume of ethylbenzene on the modified alumina adsorbent (without post-heating treatment). Salt loading: 1, 0% (w/w); 2, 5% (w/w); 3, 10% (w/w). W_p = weight of salt-modified adsorbent packed into the column.

reduced. On the modified alumina adsorbent pre-heated at 1000°C, a good peak resolution was achieved with improved peak shape.

Fig. 3 shows the dependence of the retention volume of ethylbenzene on the pre-heating temperature for each salt loading. A dependence of the retention volume on salt loading is seen on the modified alumina adsorbent pre-heated at a temperature below 900°C, but not above this, the retention volume was almost constant up to about 600°C and decreased linearly with pre-heating temperature above this.

Solute retention volume was proportional to the total surface area of the adsorbent packed into the column for modified alumina adsorbents pre-heated at a temperature below 950°C, but not on those pre-heated at a temperature above 1000°C (Fig. 4).

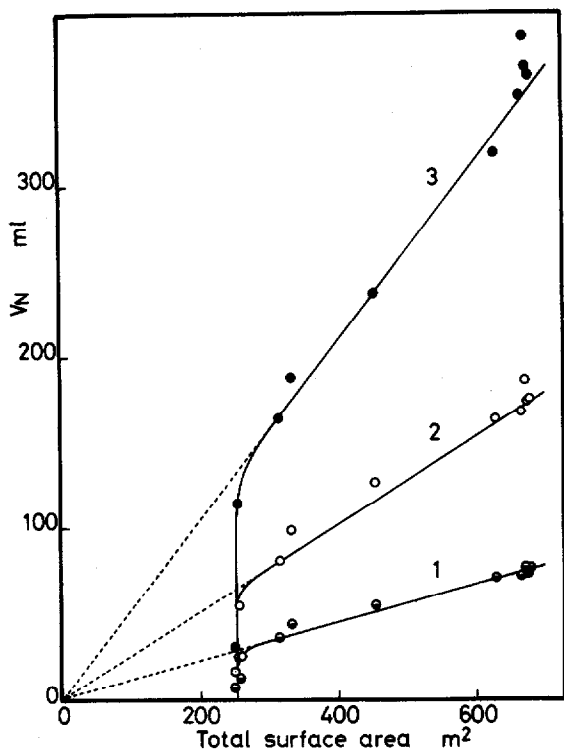


Fig. 4. Dependence of solute retention volume on the total surface area of adsorbent packed into the column. Adsorbent: modified alumina pre-heated at various temperatures (180, 400, 500, 600, 700, 800, 900, 950, 1000, 1050 and 1100°C) and coated with 5% (w/w) K_2HPO_4 (without post-heating treatment). Solutes: 1, benzene; 2, toluene; 3, ethylbenzene.

From the observed relationships, distribution constants for adsorption could be calculated for each solute and are listed in Table I. These values are similar to the values, K_A , obtained previously on a monolayer of potassium carbonate⁶. In this examination, dipotassium hydrogen phosphate may be dispersed on the alumina surface without further changes because the modified adsorbent was dried only at 180°C after salt coating. From the salt loading applied and the specific surface area of the adsorbent, it is probable that the alumina surface is completely covered with a monolayer of dipotassium hydrogen phosphate. A further decrease in specific surface area, observed on the adsorbent pre-heated at a temperature higher than 1000°C, is caused by crystallization of alumina particles due to a phase transition from the γ - to the α -form. But the total amount of the adsorbent packed into the column increased with increasing pre-heating temperature, because the particle size of the alumina decreased upon sintering and/or crystallization. In such a case, a constant total surface area of the adsorbent packed into the column was thus realized. Solute retention volume was independent of the specific surface area of the adsorbent, but was dependent on the adsorptive interaction between the solute and the adsorbent surface.

Fig. 5 shows that, regardless of the salt loading, only one curve was obtained by plotting solute retention volume against the total weight of the free alumina packed into the column. This curve has two linear parts intersecting near the tem-

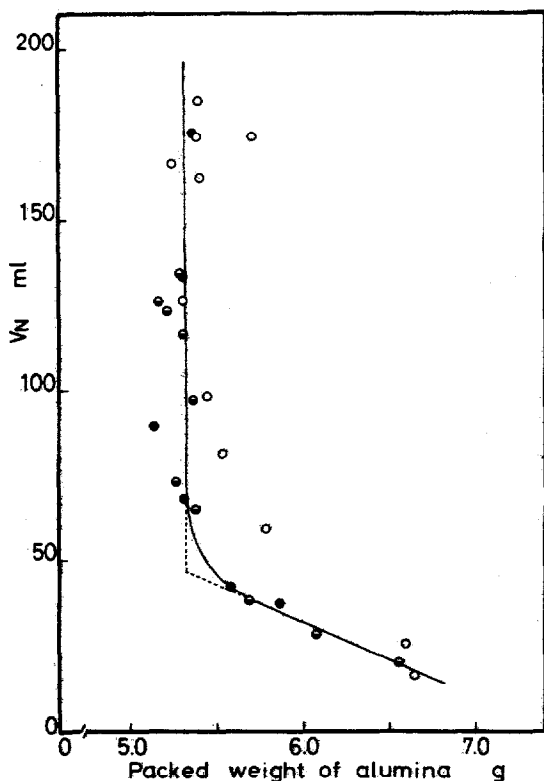


Fig. 5. Dependence of the retention volume of toluene on the total weight of free alumina packed into the column. Salt loading: ●, 0% (w/w); ○, 5% (w/w); ◐, 10% (w/w).

perature of the phase transition of alumina from the γ - to the α -form. This suggests that the dependence of the retention volume on pre-heating temperature is much influenced by sintering and/or crystallization of the alumina particle. When the modified alumina adsorbent was pre-heated at a temperature below 950°C , the total weight of the free alumina packed into the column was almost constant. Under these con-

TABLE I

DISTRIBUTION CONSTANTS FOR ADSORPTION (10^{-5} cm) ON THE SURFACE OF A MONOLAYER OF DIPOTASSIUM HYDROGEN PHOSPHATE

<i>Solute</i>	<i>Distribution constant</i>
Benzene	1.1
Toluene	2.7
Ethylbenzene	5.4
<i>p</i> -Xylene	6.0
<i>m</i> -Xylene	6.0
<i>o</i> -Xylene	7.1
<i>n</i> -Pentane	2.1
Cyclohexane	5.4
<i>n</i> -Hexane	7.0

ditions, the particle size of the alumina decreased little, but the specific surface area was gradually reduced. At a fixed salt loading, such a gradual decrease in specific surface area resulted in a progressive increase in the amount of salt per unit surface area of the free alumina. The alumina surface could be covered successively with a monolayer and with a double layer of the salt, resulting in a gradual decrease in specific surface area of the modified alumina adsorbent. It is likely that the surfaces of the monolayer and of the double layer show the same adsorptive interaction toward solute molecules. Thus, solute retention volume is proportional to the specific surface area of the adsorbent in this case.

On the other hand, the total weight of the free alumina packed into the column increased with the pre-heating temperature above 1000°C. In this temperature range, the alumina particle size was reduced, mainly by crystallization due to the phase transition of the alumina. The amount of salt per unit surface area of the free alumina increased further with decreasing specific surface area. In this case, the alumina surface could be covered with a crystalline layer formed by deposition of an excess of the salt after complete coverage with a monolayer and with a double layer. Under these conditions, the surface of the modified alumina adsorbent involves two or three types of subsurfaces present in different proportions depending upon the pre-heating temperature. These different distributions of two or three types of subsurfaces induced different specific surface areas of the modified alumina adsorbents and different adsorptive interactions toward solute molecules. A linear decrease in solute retention volume with the total weight of the free alumina packed into the column was caused mainly by a decrease in the adsorptive interaction of the adsorbent surface toward the solute molecules. The dependence of the retention volume on pre-heating temperature can be understood on the basis of the different distributions of the subsurfaces depending on the amount of the salt per unit surface area of the free alumina. It should be noted that the true effect of the pre-heating treatment on the retention volume could be revealed by use of the total weight of the free alumina packed into the column as a parameter for describing the characteristics of the GSC column.

Fig. 6 shows some chromatograms of a mixture of benzene, toluene, ethylbenzene, *o*-, *m*- and *p*-xylenes obtained by GSC on the modified alumina adsorbent coated with dipotassium hydrogenphosphate (5%, w/w). Without post-heating treatment, each solute gave an asymmetric peak with a long retention time. Post-heating effected a reduction in retention time and an improved peak shape, but a poor peak resolution between xylene isomers. The last observation is in contrast to a previous result obtained on a modified alumina adsorbent coated with tripotassium phosphate⁴, and is probably caused by the different chemical properties of the salts.

Fig. 7 shows the curve obtained, regardless of pre-heating temperature, by plotting the retention volume of toluene against the total weight of the free alumina packed into the column. By extrapolation, the two linear parts intersect near the melting point of potassium pyrophosphate (1109°C). This suggests that a layer of potassium pyrophosphate is formed on the alumina surface and that the adsorption equilibrium on the surface of this layer contributes significantly to solute retention. We could not confirm the formation of potassium pyrophosphate and obtain any information about the chemical changes of the salt on the alumina, because the X-ray diffraction patterns of the modified alumina adsorbents showed only peaks of γ -alumina and/or α -alumina. It may be that potassium pyrophosphate is dispersed

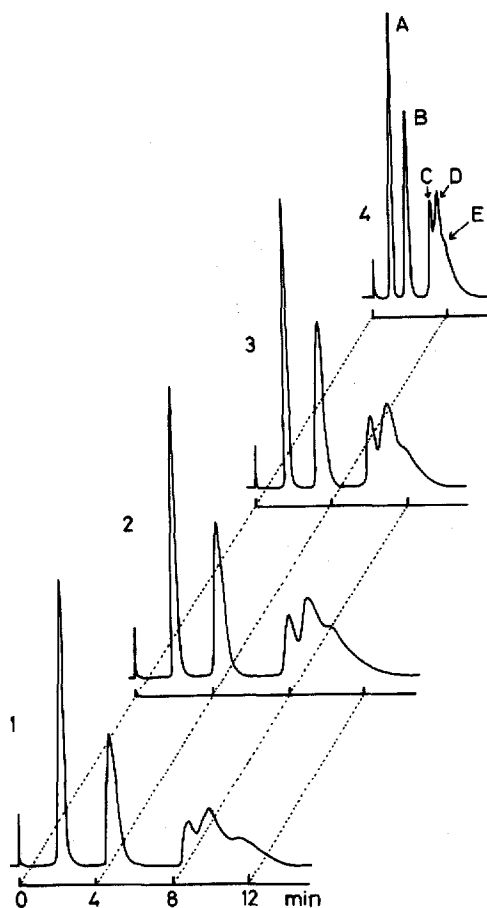


Fig. 6. Chromatograms of an aromatic hydrocarbon mixture obtained by GSC on the modified alumina adsorbent coated with 5% (w/w) K_2HPO_4 and post-heated at various temperatures (without pre-heating treatment). Post-heating temperature: 1, without post-heating; 2, 900°C; 3, 1000°C; 4, 1100°C. Solutes as in Fig. 2.

as fine crystalline particles or as a thin crystalline layer on the alumina surface.

In the case of post-heating treatment below the melting point of potassium pyrophosphate, it is probable that the alumina particle size is slightly changed and the specific surface area of the base alumina can be varied through disappearance of narrow pores due to a slight degree of sintering. Under these conditions, it is likely that potassium pyrophosphate, formed *in situ* from dipotassium hydrogenphosphate by pyrolysis, covered the alumina surface as fine crystalline particles. Such a change would result in a reduction of the surface area available for adsorption of hydrocarbon solutes in GSC, but would have little influence on the adsorptive interaction of the adsorbent surface toward solute molecules. In the case of post-heating treatment above the melting point of potassium pyrophosphate, the alumina surface can be first covered uniformly with a fused salt layer and, after cooling, with a thin crystalline layer of this salt formed through regular recrystallization. The particle size and specific surface area of the base alumina were significantly decreased with a large

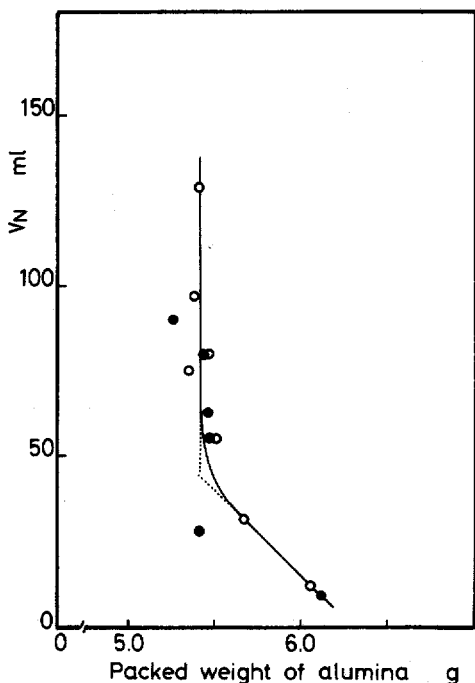


Fig. 7. Dependence of the retention volume of toluene on the total weight of free alumina packed into the column. Pre-heating temperature: \circ , 700°C; \bullet , 900°C.

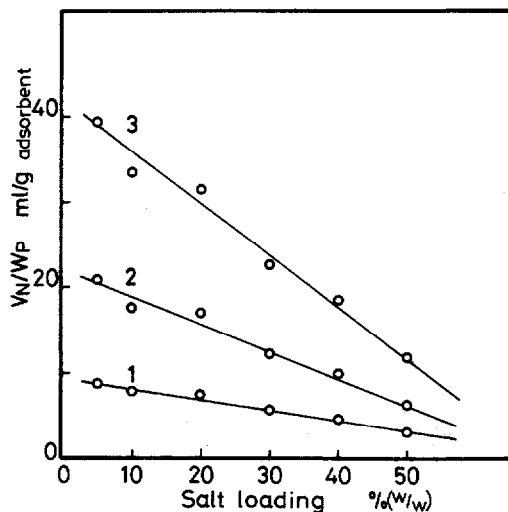


Fig. 8. Dependence of solute retention volume on salt loading on the modified alumina adsorbent without pre-heating treatment and post-heated at 900°C. Solutes: 1 = benzene; 2 = toluene; 3 = ethylbenzene.

degree of sintering and/or crystallization of alumina particles due to the phase transition. Such large changes induced correspondingly large influences in the specific surface area of the modified alumina adsorbent and the adsorptive interaction of the surface toward solute molecules. Thus, the effects of post-heating treatment on solute retention volume can be also understood by taking account of changes in the particle size of the base alumina with post-heating temperature.

The retention volume of some solutes decreased with increasing salt loading as shown in Fig. 8, and was proportional to the specific surface area of the modified alumina adsorbent used. From the salt loading applied, it is reasonable to consider that the alumina surface was almost completely covered with a crystalline layer of the salt. Dipotassium hydrogen phosphate coated was thoroughly converted into potassium pyrophosphate during post-heating treatment at 900°C. In this case, an adsorption equilibrium on the crystalline layer of potassium pyrophosphate contributed exclusively to the solute retention. The proportionality constant, calculated from the linear relationship between the retention volume and the specific surface area, corresponded to the distribution constant for adsorption on such a surface (Table II). The values obtained are about twice as large as those obtained on a crystalline layer of potassium carbonate and can be regarded as acceptable when allowance is made for the different method used for determination of the specific surface area of the adsorbent.

TABLE II
DISTRIBUTION CONSTANTS FOR ADSORPTION (10^{-5} cm) ON THE SURFACE OF THE CRYSTALLINE LAYER OF POTASSIUM PYROPHOSPHATE

<i>Solute</i>	<i>Distribution constant</i>
Benzene	1.4
Toluene	3.0
Ethylbenzene	5.7
<i>p</i> -Xylene	6.5
<i>m</i> -Xylene	6.3
<i>o</i> -Xylene	7.3
<i>n</i> -Pentane	1.9
Cyclohexane	3.8
<i>n</i> -Hexane	5.4

In the present case, we observed that the total amount of the modified alumina adsorbent packed into the column increased linearly with the salt loading, but the total weight of free alumina in the column was almost constant. From this, it can be concluded that the free alumina can be regarded as a solid support and the salt coated as a stationary phase in gas-liquid chromatography (GLC). The process of modification of the active adsorbent with the salt is very similar to the deactivation of a solid support for GLC with a polar liquid phase.

All the results could be understood on the basis of the different distributions of the salt coated on the alumina, and the amount of the salt per unit surface area of the base material.

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