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

SALT LOADING DEPENDENCE OF RETENTION VOLUME ON MODIFIED ALUMINA ADSORBENT COATED WITH POTASSIUM CARBONATE

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SUMMARY

The retention mechanism in gas-solid chromatography has been studied for alumina adsorbents modified by pre-heating and subsequent coating with various amounts of potassium carbonate. Four salt loading regions could be characterized. The salt loading dependence of the specific surface area of the modified adsorbent could be approximated as a linear relation. A model for the salt-modified adsorbent surface is described in which the base alumina adsorbent surface is gradually covered with two types of salt layers, first a monolayer and secondly a crystalline layer. The solute retention in gas-solid chromatography could be interpreted on the basis of a linear combination of concurrent contributions from adsorption equilibria on sub-surfaces distributed on the adsorbent. Acceptable results were obtained through analysis of experimental data.

INTRODUCTION

The coating of adsorbents with various inorganic salts in order to improve their surface properties for gas-solid chromatography (GSC) has been extensively studied¹⁻¹¹. Such salt-modified adsorbents with desirable surface properties are expected to be easily prepared by controlling the nature of the inorganic salt and its loading, and by adjusting the temperature of the thermal treatments before and after coating. Many investigations have concentrated on the effects of fixed loadings of various inorganic salts on the retention data. In such cases the solute retention has

been successfully interpreted in terms of contributions from two types of intermolecular interactions, non-specific and specific, between the solute molecule and the adsorbent surface³⁻⁶. It is also generally accepted that salt-modified adsorbents exhibit adsorptive characteristics of both the surface of the inorganic salt and that of the original adsorbent, even when the latter is completely covered with several layers of salt^{1,3}. However, the surface properties of salt-modified adsorbents have not yet been systematically related to the salt loading.

It is reasonable to consider that, depending on the salt loading, the original adsorbent surface is gradually converted into a less active one, the active adsorption sites being increasingly occupied by the salt dispersed in the forms of ions and/or ion-pairs or shielded with a new layer formed by reaction or with fine particles or thin films of the salt crystals. Some surface properties of the salt-modified adsorbent, *e.g.*, specific surface area and surface adsorption activity, are expected to reflect the different distributions of the salt coated on the adsorbent surface.

This paper is concerned with establishing the exact nature of salt-modified adsorbents in order further to understand solute retention in GSC. It is particularly important to determine the quantitative relationship between salt loading and solute retention volume or the specific surface area on the basis of an exact model of the surface of the salt-modified adsorbent.

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 an extra pure grade of potassium carbonate as a modifier. Before coating, the alumina was pre-heated for 2 h at a temperature of 500, 700, 900 or 1000°C in order to control the specific surface area and adsorption activity. Ten grams of the alumina were then added to a solution containing 0.05–3.0 g of potassium carbonate in 20 ml of distilled water, and the mixture was allowed to stand overnight. The mixture was then evaporated to dryness on a water-bath with occasional stirring. The adsorbent with zero salt loading was prepared in the same way but by using distilled water instead of the potassium carbonate solution. The salt-modified adsorbents were dried for 3 h at 180°C before use and packed into a stainless-steel column (100 × 0.3 cm I.D.).

A Hitachi 063 gas chromatograph equipped with a thermal conductivity detector and a Hitachi 056 recorder was used throughout. Helium was used as the carrier gas at a flow-rate of 40 ml/min. 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. Columns packed with the adsorbent were pre-conditioned for 2 h at 200°C and then for another 2 h at 180°C in a helium gas stream. After the appearance of a stable baseline, the sample was injected into the column with a Terumo MST 10 microsyringe.

The procedures for measurement and correction of solute retention volumes were as described previously¹¹. The specific surface areas of these adsorbents were measured by the BET method of nitrogen adsorption at liquid nitrogen temperature. The loading of potassium carbonate was calculated from the amount added, since such values were in agreement with those evaluated from the potassium content in the adsorbent determined as potassium perchlorate by gravimetry.

RESULTS AND DISCUSSION

The GSC retention volume of toluene as solute on the alumina adsorbents coated with potassium carbonate gradually decreased to a fixed value with increasing salt loading (Fig. 1). The curves in Fig. 1 are characterized by a large decrease in retention volume at lower salt loadings. A similar decrease has been observed on silica gels modified with copper complex salts⁷. The specific surface area of the salt-modified adsorbents showed a somewhat different variation (Fig. 2) from that of the retention volume. This suggests that solute retention volume on salt-modified adsorbents depends not only upon the specific surface area but also on the surface adsorption activity.

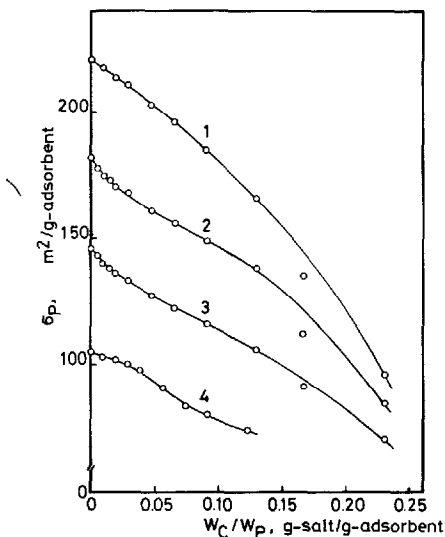
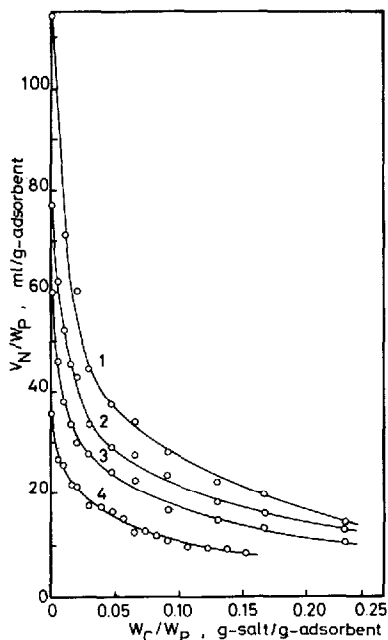


Fig. 1. Retention volume of toluene on salt-modified alumina adsorbents coated with potassium carbonate. Column temperature: 180°C. Adsorbents pre-heated at 500°C (1), 700°C (2), 900°C (3) and 1000°C (4).

Fig. 2. Specific surface area of salt-modified alumina adsorbents coated with potassium carbonate. Adsorbents as in Fig. 1.

Considering only one adsorption equilibrium with a linear isotherm for distribution of the solute between the gas and solid phases in a GSC column, the retention volume of a solute can be described by applying basic retention theory

$$V_N = K_S A_P \quad (1)$$

or

$$V_N/W_P = K_S \sigma_P \quad (2)$$

where V_N is the net retention volume of the solute, K_S a distribution constant for adsorption, A_p and W_p are the total surface area and total weight of the adsorbent packed into the column and σ_p is the specific surface area of the salt-modified adsorbent, respectively. The K_S value calculated from eqn. 1 or 2 can be used for evaluating the surface adsorption activity of the adsorbent, *i.e.*, the interaction between the solute molecule and the adsorbent surface.

In Fig. 3 the results shown in Figs. 1 and 2 are re-plotted according to eqn. 2. The K_S value for the solute, obtained as the slope of a straight line passing through the origin and each observed point, is dependent on the salt loading. The plots comprised curves consisting of three different parts: in the first part the retention volume varied significantly with a slight change in specific surface area; in the second part the retention volume changed in proportion to the specific surface area and the third part is the transitional region connecting the first and second parts.

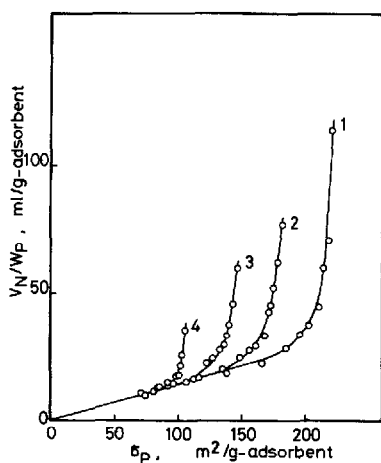


Fig. 3. Dependence of retention volume of toluene upon specific surface area. Column temperature: 180°C. Adsorbents as in Fig. 1.

For the first part of the V_N/W_p vs. σ_p curves, corresponding with lower salt loadings, active sites with high adsorption activity on the original alumina surface can be anticipated to be occupied, probably by adsorption, with potassium carbonate dispersed in the form of ions and/or ion-pairs. It is most probable that, with increasing salt loading, a new surface layer of potassium carbonate with low adsorption gradually covers the original alumina surface. The method of deactivation is very similar to that of a solid support gradually covered by a monolayer of the liquid phase at low liquid loadings¹². The new surface layer may correspond to the dense monolayer of salt mentioned by Gavrilina *et al.*⁸.

After complete shielding of the original alumina surface with the new monolayer, further potassium carbonate is considered to precipitate as fine particles or as thin crystalline films and gradually covers the deactivated alumina surface. This situation corresponds to the transitional part of the curves in Fig. 3.

When the whole of the deactivated alumina surface is covered with fine particles or thin films of the potassium carbonate, increasing salt loading results in an

increase in the thickness of the surface layer of the salt and a subsequent decrease in the specific surface area of the salt-modified adsorbent. In Fig. 3, all the observed points corresponding to this region fell on one straight line, regardless of the initial pre-heating of the alumina. This result indicates that, at higher salt loadings, the solute retention volume is determined chiefly by the adsorption equilibrium on the surface of the fine particles or thin films of the potassium carbonate. The K_s value, calculated as the slope of the straight line in Fig. 3, corresponds to a distribution constant of adsorption (K_C) for each solute on such a surface of potassium carbonate (Table I).

TABLE I

DISTRIBUTION COEFFICIENT OF THE SOLUTE CALCULATED FROM THE SLOPE OF THE STRAIGHT LINE IN FIG. 3

Column temperature: 180°C for aromatic hydrocarbons; 80°C for aliphatic hydrocarbons.

Solute	K_C (cm) · 10 ⁵
Benzene	0.66
Toluene	1.4
Ethylbenzene	2.7
<i>p</i> -Xylene	3.1
<i>m</i> -Xylene	3.2
<i>o</i> -Xylene	3.6
<i>n</i> -Pentane	1.2
Cyclohexane	2.7
<i>n</i> -Hexane	3.9

A similar relationship between solute retention volume and the specific surface area of the adsorbent has been found for refined adsorbents with energetically homogeneous surfaces, such as graphitized carbon black and Spherosil^{4,13}.

For analysis of the GSC retention volumes of the solutes the procedure of Conder *et al.*¹⁴ was applied with some modifications, neglecting the contribution of the partition equilibrium because of the absence of a bulk liquid phase and substituting the amount of the salt loaded, W_C , for that of the liquid phase coated, V_L . Fig. 4 shows that a plot of V_N/W_C against W_S/W_C had four linear parts with different slopes and intercepts for each solute (W_S = total weight of salt-free adsorbent packed into the column). This result is very similar to one obtained previously¹². The salt loading at the intersection point of any two of the adjacent straight lines is almost constant for all solutes studied (Table II).

The numbers of moles of potassium carbonate per unit surface area of the original alumina, calculated from the values of W_{C1}/W_S , W_{C0}/W_S and W_{C2}/W_S , were 0.3, 1.1 and 4.4 $\mu\text{mol}/\text{m}^2$, respectively. From these values, it is reasonable to regard W_{C0}/W_S and W_{C2}/W_S as the requirements for complete coverage with potassium carbonate dispersed in the form of ions and/or ion-pairs, and of fine particles or thin crystalline films, respectively. Supposing previously¹² that the original alumina surface consists of at least two different subsurfaces with higher and lower adsorption activities, the value of W_{C1}/W_S can be regarded as the requirement for covering the

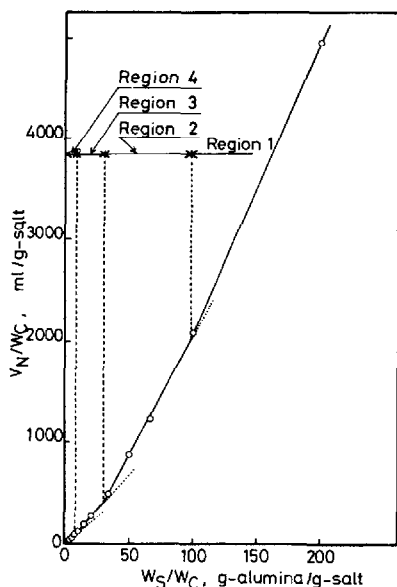


Fig. 4. Plots of V_N/W_C vs. W_S/W_C for benzene. Column temperature: 180°C. Salt-modified alumina adsorbent pre-heated at 700°C.

whole of the subsurface of higher adsorption activity with a monolayer of potassium carbonate.

According to the procedure of Rudzinski and his co-workers¹⁵, the original surface of the alumina pre-heated at 1000°C was confirmed to contain two energetically different subsurfaces with adsorption energies of *ca.* 9.5 and < 8 kcal/mol. Thus, attention is now focused on finding the quantitative correlation between solute retention volume, adsorption contributions on subsurfaces, specific surface area of the salt-modified adsorbent and salt loading. Fortunately, in gas-liquid chromatogra-

TABLE II

SALT LOADINGS AT THREE INTERSECTION POINTS BETWEEN TWO ADJACENT LINEAR CURVES IN FIG. 4

Solute	W_{C1}/W_S (%o, w/w)				W_{C0}/W_S (%o, w/w)				W_{C2}/W_S (%o, w/w)			
	500°C	700°C	900°C	1000°C	500°C	700°C	900°C	1000°C	500°C	700°C	900°C	1000°C
Benzene	1.00	0.66	0.50	0.51	3.17	2.91	1.71	1.91	11.9	13.2	9.48	7.11
Toluene	1.00	0.72	0.50	0.52	3.24	3.14	1.76	2.00	11.3	13.1	9.29	7.00
Ethylbenzene	—	0.73	0.50	0.52	3.35	3.03	1.78	2.00	11.3	10.4	9.57	6.98
<i>p</i> -Xylene	—	0.51	0.50	0.51	3.23	3.09	1.68	2.01	11.0	11.6	9.58	6.99
<i>m</i> -Xylene	—	0.63	0.50	0.52	3.07	3.16	1.77	2.00	10.9	10.9	10.04	7.00
<i>o</i> -Xylene	—	0.56	0.51	0.51	3.80	3.14	1.77	2.00	11.0	11.0	8.28	6.98
<i>n</i> -Pentane	1.00	1.05	0.48	0.53	3.53	3.05	2.26	2.00	11.1	11.5	9.65	7.03
Cyclohexane	—	—	0.50	0.51	3.75	3.43	1.78	2.03	11.0	11.3	9.65	7.00
<i>n</i> -Hexane	—	0.79	0.50	0.51	3.27	3.08	1.95	2.00	10.9	11.2	9.29	7.00

phy, solute retention volume can gradually be described as a linear combination of the contributions from concurrent absorption and adsorption equilibria. The GSC retention volume can also be written as a linear combination of possible concurrent contributions from adsorptions on subsurfaces with different adsorption activities

$$V_N = \sum_i K_i A_i \quad (3)$$

where K_i is an intrinsic distribution coefficient for adsorption on the subsurface i and A_i is the total surface area of the subsurface i existing on the adsorbent packed into the column. The total surface area of the salt-modified adsorbent packed into the column can be written as:

$$A_s = \sum_i A_i \quad (4)$$

Then, the apparent adsorption activity of the salt-modified adsorbent can be expressed as:

$$K_{ad} = \frac{\sum_i K_i A_i}{\sum_i A_i} \quad (5)$$

The change in adsorptivity of the salt-modified adsorbent can thus be correlated with the variation in distributions of subsurfaces of different adsorption activities on the alumina surface with the salt loading. The ranges of salt loading corresponding to each straight line in Fig. 4 are now denoted regions 1, 2, 3 and 4 in order of increasing loading. Regions 1 and 2 correspond to the first part of the V_N/W_p vs. σ_p curves in Fig. 3, region 3 to the transitional part and region 4 to the second part, respectively.

In region 1, subsurface 1 (surface area: $A_1 = \sigma_1 W_s$) with higher adsorption activity is considered to be partly covered with potassium carbonate dispersed in the form of ions and/or ion-pairs. The deactivated surface is formed by preferential blocking of the originally active adsorption sites on subsurface 1 with potassium carbonate. The original alumina surface is assumed, as mentioned above, to contain two different subsurfaces, 1 and 2 (surface area: $A_2 = \sigma_2 W_s$; with lower adsorption activity). The total surface area of the base alumina, $A_s^0 = \sigma_s^0 W_s$, is equal to the sum of the surface areas of subsurfaces 1 and 2, *i.e.*, $A_1 + A_2$. Using the surface area of subsurface 1 covered with potassium carbonate dispersed in the form of ions and/or ion-pairs, A_{sc} , and that of the deactivated surface, A_{cm} , the total surface area of the salt-modified adsorbent packed into the column can be written (from eqn. 4) as:

$$A_s = (A_1 - A_{sc}) + A_{cm} + A_2 \quad (6)$$

Considering that both surface areas A_{sc} and A_{cm} are proportional to the amount of potassium carbonate loaded, W_c , they can be written as $A_{sc} = \alpha W_c$ and $A_{cm} = \beta W_c$. The proportionality factors, α and β , are expected to be constant for a particular inorganic salt-solid adsorbent pair, regardless of the nature of the solute. Substituting these relations into eqn. 6, the following equation can be derived

$$A_S = A_S^0 - (\alpha - \beta)W_C \quad (7)$$

which using the relation $\sigma_S = A_S/W_S$, can be rewritten as:

$$\sigma_S = \sigma_S^0 - (\alpha - \beta)(W_C/W_S) \quad (8)$$

In this region, the solute retention can be expected to be subject to contributions from adsorption equilibria on subsurface 1 (surface area: $A_1 - A_{SC}$), subsurface 2 (A_1) and the deactivated surface (A_{CM}). The solute retention volume can then be expressed as

$$V_N = K_1(A_1 - A_{SC}) + K_2A_2 + K_A A_{CM} \quad (9)$$

where K_1 , K_2 and K_A are intrinsic distribution coefficients on the subsurfaces 1 and 2 and on the deactivated surface, respectively and their order of magnitude is $K_1 > K_2 > K_A$. The apparent adsorptivity of the original alumina surface, equal to the retention volume of any solute at zero salt loading, V_{N0} , can be now rewritten from eqn. 5:

$$V_{N0} = K_{ad}^0 A_S^0 = K_1 A_1 + K_2 A_2 \quad (10)$$

Therefore, eqn. 9 can be rearranged

$$V_N/W_S = K_{ad}^0 \sigma_S^0 - (\alpha K_1 - \beta K_A)(W_C/W_S) \quad (11)$$

and

$$V_N/W_C = -(\alpha K_1 - \beta K_A) + K_{ad}^0 \sigma_S^0 (W_S/W_C) \quad (12)$$

If $\alpha > \beta$, these equations can be interpreted in terms of the decrease in the experimental retention volume and specific surface area with increasing salt loading.

In region 2, the deactivated surface is regarded as extending to subsurface 2 after complete coverage of subsurface 1. On subsurface 2 the deactivated surface is assumed to show the same adsorption activity as that on subsurface 1, and the proportionality factors, α and β , are considered to be the same as those for region 1. In this region, eqns. 7 and 8 are again valid. Considering that the effects of adsorption equilibria on subsurface 2 [surface area: $A_2 - (A_{SC} - A_1)$] and the deactivated surface (A_{CM}) contribute to solute retention, the solute retention volume can be expressed as:

$$V_N = K_2[A_2 - (A_{SC} - A_1)] + K_A A_{CM} \quad (13)$$

By using the relations $A_{SC} = \alpha W_C$ and $A_{CM} = \beta W_C$, eqn. 13 can be rewritten as

$$V_N/W_S = K_2 \sigma_S^0 - (\alpha K_2 - \beta K_A)(W_C/W_S) \quad (14)$$

and

$$V_N/W_C = -(\alpha K_2 - \beta K_A) + K_2 \sigma_S^0 (W_S/W_C) \quad (15)$$

These equations fit the experimental results obtained in this region.

In region 3, potassium carbonate provides further coverage as fine particles or thin crystalline films precipitated on the deactivated surface with which the base alumina surface is completely shielded. The surface area of the fine particles or thin films, A_C , and that of the deactivated surface covered with them, A_{CB} , are simply considered to be proportional to the amount of potassium carbonate

$$A_C = \beta'(W_C - W_{C0}) \tag{16}$$

$$A_{CB} = \alpha'(W_C - W_{C0}) \tag{17}$$

where α' and β' are proportionality factors. The latter are expected to be constant for a particular inorganic salt–solid adsorbent pair, regardless of the nature of the solute. Then, the surface area of the salt-modified adsorbent, measured by the BET method, can be written as:

$$A_S = (A_{CM}^0 - A_{CB}) + A_C \tag{18}$$

Substituting eqns. 16 and 17 into the above equation, we obtain

$$A_S = A_{CM}^0 + (\alpha' - \beta')W_{C0} - (\alpha' - \beta')W_C \tag{19}$$

and

$$\sigma_S = \sigma_{CM}^0 + (\alpha' - \beta')(W_{C0}/W_S) - (\alpha' - \beta')(W_C/W_S) \tag{20}$$

where W_{C0} is the amount of potassium carbonate for complete coverage of the original alumina surface as ions and/or ion-pairs and A_{CM}^0 is the surface area of the deactivated surface shielding completely the original alumina surface ($A_{CM}^0 = \beta W_{C0}$). In this region, two adsorption equilibria on the deactivated surface (surface area: $A_{CM}^0 - A_{CB}$) and on the surface of the fine particles or thin films of potassium carbonate (A_C) are thought to take part in the solute retention. The solute retention volume can be written in the form:

$$V_N = K_A(A_{CM}^0 - A_{CB}) + K_C A_C \tag{21}$$

Then

$$V_N/W_S = K_A \sigma_{CM}^0 + (\alpha' K_A - \beta' K_C)(W_{C0}/W_S) - (\alpha' K_A - \beta' K_C)(W_C/W_S) \tag{22}$$

and

$$V_N/W_C = -(\alpha' K_A - \beta' K_C) + [K_A \sigma_{CM}^0 + (\alpha' K_A - \beta' K_C)(W_{C0}/W_S)](W_S/W_C) \tag{23}$$

where K_C , which is less than K_A , is an intrinsic distribution coefficient for adsorption on the surface of the fine particles or thin films of potassium carbonate and $\sigma_{CM}^0 = A_{CM}^0/W_S$.

In region 4, the deactivated surface is completely covered with the fine particles or thin films of potassium carbonate, the thickness of which increases with increasing salt loading. A_C^0 , equal to $\beta'(W_{C2} - W_{C0})$, is the total surface area of potassium carbonate just shielding the whole of the deactivated surface. The surface area of a new layer of fine particles or thin films and that of the foundation layer covered with them are assumed to be proportional to the amount of potassium carbonate:

$$A'_C = \beta''(W_C - W_{C2}) \quad (24)$$

$$A'_{CB} = \alpha''(W_C - W_{C2}) \quad (25)$$

The surface area of the salt-modified adsorbent, in this region, can be expressed as

$$A_S = A_C^0 - A'_{CB} + A'_C \quad (26)$$

and therefore:

$$A_S = A_C^0 + (\alpha'' - \beta'')W_{C2} - (\alpha'' - \beta'')W_C \quad (27)$$

Provided that the distribution coefficients for adsorption on both surfaces of the fine particles or thin films of potassium carbonate are equal, the solute retention volume can be written in the form

$$V_N = K_C A_C \quad (28)$$

and substituting eqn. 27 into eqn. 28 we obtain:

$$V_N = K_C [A_C^0 + (\alpha'' - \beta'')W_{C2} - (\alpha'' - \beta'')W_C] \quad (29)$$

Then

$$V_N/W_S = K_C [\sigma_C^0 + (\alpha'' - \beta'')(W_{C2}/W_S)] - (\alpha'' - \beta'')K_C(W_C/W_S) \quad (30)$$

and:

$$V_N/W_C = -(\alpha'' - \beta'')K_C + K_C [\sigma_C^0 + (\alpha'' - \beta'')(W_{C2}/W_S)](W_S/W_C) \quad (31)$$

With the equations derived as above, on the basis of the distributions of potassium carbonate on the alumina surface with increasing salt loading, the solute retention volume in GSC on the salt-modified adsorbent and the specific surface area can be now determined as linear functions of the salt loading by the least-squares regression method. All of the unknown constants involved in these equations can be determined from the slopes and the intercepts at the three intersection points listed in Table II. The resulting values are given in Tables III–VII.

As expected, the solute distribution coefficients for adsorption on the sub-surface 1 (K_1), on the subsurface 2 (K_2), on the deactivated surface (K_A) and on the surface of the fine particles or thin films of potassium carbonate (K_C) lie in the order

TABLE III

DISTRIBUTION COEFFICIENTS FOR ADSORPTION ON SALT-MODIFIED ALUMINA ADSORBENT PRE-HEATED AT 500°C

Solute	$K_1 (cm) \cdot 10^5$	$K_2 (cm) \cdot 10^5$	$K_A (cm) \cdot 10^5$			$K_C (cm) \cdot 10^5$		
			Region 1	Region 2	Region 3	Intercept*	Slope*	Slope**
Benzene	2.2	1.5	0.83	0.83	0.85	0.66	0.66	0.66
Toluene	8.2	3.8	2.0	2.0	2.0	1.4	1.3	1.4
Ethylbenzene	—	8.8	—	4.2	4.1	2.8	3.0	2.7
<i>p</i> -Xylene	—	9.4	—	4.4	4.4	3.1	3.3	3.1
<i>m</i> -Xylene	—	9.3	—	4.1	4.4	3.2	3.3	3.2
<i>o</i> -Xylene	—	10.6	—	5.9	5.2	3.2	3.0	3.6
<i>n</i> -Pentane	4.7	4.2	2.0	2.0	1.9	1.3	1.2	1.2
Cyclohexane	—	10.4	—	5.1	4.4	2.8	3.0	2.7
<i>n</i> -Hexane	—	15.1	—	7.5	7.5	4.0	4.4	3.9

* Calculated from the slope and intercept of the straight line in region 4.

** From Table I.

$K_1 > K_2 > K_A > K_C$. The distribution coefficient K_A of each solute determined in three different regions was approximately constant, as was K_C calculated from the slope and the intercept of the regression curve of region 4. Thus, satisfactory results were obtained through analysis of the experimental data with the equations derived here, so that the model chosen can be considered to be valid for distributions of potassium carbonate on alumina.

It is surprising that the high adsorption activity of subsurface 1, K_1 , and low activity of subsurface 2, K_2 , are effectively reduced to the same activity, K_A , by only a small amount of potassium carbonate, which corresponds to monolayer coverage. It

TABLE IV

DISTRIBUTION COEFFICIENTS FOR ADSORPTION ON SALT-MODIFIED ALUMINA ADSORBENT PRE-HEATED AT 700°C

Solute	$K_1 (cm) \cdot 10^5$	$K_2 (cm) \cdot 10^5$	$K_A (cm) \cdot 10^5$			$K_C (cm) \cdot 10^5$		
			Region 1	Region 2	Region 3	Intercept*	Slope*	Slope**
Benzene	2.7	1.3	0.81	1.0	1.0	0.62	0.63	0.66
Toluene	7.1	3.4	2.3	2.1	2.4	0.93	1.2	1.4
Ethylbenzene	14.4	7.3	4.6	4.1	5.1	2.5	2.7	2.7
<i>p</i> -Xylene	15.7	8.3	1.6	4.4	5.5	2.3	2.4	3.0
<i>m</i> -Xylene	17.8	7.9	3.9	4.6	5.5	2.1	2.8	2.8
<i>o</i> -Xylene	23.0	9.1	2.5	5.4	6.5	2.8	3.3	3.6
<i>n</i> -Pentane	4.4	3.4	2.3	1.9	2.4	1.2	1.2	1.3
Cyclohexane	10.0	8.1	—	5.0	6.0	2.2	2.4	2.5
<i>n</i> -Hexane	20.0	11.8	8.7	7.3	9.8	4.0	3.8	3.9

* Calculated from the intercept and slope of the straight line in region 4.

** From Table I.

TABLE V
DISTRIBUTION COEFFICIENTS FOR ADSORPTION ON SALT-MODIFIED ALUMINA ADSORBENT
PRE-HEATED AT 900°C

Solute	$K_1 (cm) \cdot 10^5$	$K_2 (cm) \cdot 10^5$	$K_A (cm) \cdot 10^5$			$K_C (cm) \cdot 10^5$		
			Region 1	Region 2	Region 3	Intercept*	Slope*	Slope**
Benzene	2.0	1.3	0.96	0.96	0.96	0.60	0.65	0.66
Toluene	5.4	3.6	2.3	2.3	2.2	1.3	1.4	1.4
Ethylbenzene	11.2	7.2	4.5	4.5	4.4	3.1	2.8	2.7
<i>p</i> -Xylene	14.4	8.3	4.9	4.9	4.9	3.3	3.2	3.1
<i>m</i> -Xylene	17.2	7.9	4.9	4.9	4.8	3.6	3.3	3.2
<i>o</i> -Xylene	18.9	9.4	5.7	5.4	5.4	4.1	4.0	3.6
<i>n</i> -Pentane	3.7	2.8	2.0	2.1	1.8	1.4	1.2	1.2
Cyclohexane	12.7	6.0	3.8	3.8	4.4	2.8	2.4	2.7
<i>n</i> -Hexane	13.9	10.2	6.6	6.6	6.1	4.2	3.6	3.9

* Calculated from the intercept and slope of the straight line in region 4.

** From Table I.

should be noted that homogeneous surface properties could be achieved by coating the heterogeneous surface of the alumina with such a small amount of the salt. These facts suggest that coated potassium carbonate did not act as the conducting layer mentioned by Cadogan and Sawyer¹⁶ but almost completely shielded the original adsorption activity of the base alumina adsorbent. In the present work, the adsorption activity of the deactivated surface, K_A , is almost the same on all the base alumina adsorbents, which is probably due to coating with the same salt and/or to the similar adsorption activities of the alumina. The adsorption activity of the deactivated surface is, however, expected to be characterized chiefly by the salt or by the salt-base adsorbent pair.

TABLE VI
DISTRIBUTION COEFFICIENTS FOR ADSORPTION ON SALT-MODIFIED ALUMINA ADSORBENT
PRE-HEATED AT 1000°C

Solute	$K_1 (cm) \cdot 10^5$	$K_2 (cm) \cdot 10^5$	$K_A (cm) \cdot 10^5$			$K_C (cm) \cdot 10^5$		
			Region 1	Region 2	Region 3	Intercept*	Slope*	Slope**
Benzene	1.7	1.0	0.88	0.88	0.88	0.64	0.59	0.66
Toluene	5.3	2.7	2.1	2.1	2.1	1.5	1.6	1.4
Ethylbenzene	11.8	5.5	4.0	4.0	4.0	2.6	2.8	2.7
<i>p</i> -Xylene	19.7	6.8	4.4	4.4	4.3	3.0	3.4	3.1
<i>m</i> -Xylene	14.2	6.2	4.7	4.7	4.7	3.1	3.6	3.2
<i>o</i> -Xylene	18.8	7.5	4.9	4.9	4.9	3.2	3.1	3.6
<i>n</i> -Pentane	3.4	2.2	1.5	1.4	1.4	1.1	1.1	1.2
Cyclohexane	9.5	4.9	3.2	3.2	3.2	2.1	2.2	2.5
<i>n</i> -Hexane	17.1	7.7	4.8	4.8	4.8	3.2	4.1	3.9

* Calculated from the intercept and slope of the straight line in region 4.

** From Table I.

TABLE VII

PROPORTIONALITY FACTORS (m^2/g SALT) AND THEIR DIFFERENCES

Pre-heating temperature of alumina ($^{\circ}C$)	$\alpha \cdot 10^{-3}$	$\beta \cdot 10^{-3}$	$(\alpha - \beta) \cdot 10^{-2}$	$\alpha' \cdot 10^{-3}$	$\beta' \cdot 10^{-3}$	$(\alpha' - \beta') \cdot 10^{-2}$	$(\alpha'' - \beta'') \cdot 10^{-2}$
500	6.64	6.49	1.50	2.80	2.62	1.80	4.07
700	6.09	5.72	3.16	2.01	1.91	1.00	2.84
900	8.11	7.61	4.00	1.79	1.64	1.50	1.64
1000	5.25	5.20	0.50	2.08	1.88	1.95	2.08

Fig. 5 shows the different distributions of subsurfaces on the alumina surface, as determined by the present analysis.

The specific surface area of the original alumina adsorbent decreased with increasing pre-heating temperature, but the ratios of subsurfaces 1 and 2 to the total surface of the alumina were almost constant (Table VIII). Although the ratios K_1/K_2 and σ_1/σ_2 were kept almost constant regardless of pre-heating temperature, the absolute values K_1 , K_2 , σ_1 and σ_2 tended to decrease with increasing pre-heating temperature. We therefore concluded that the adsorption capacity of each subsurface on the alumina decreased with increasing pre-heating temperature, but that the proportional contribution from each subsurface to the total surface was hardly affected, *i.e.*, the energetical distribution for the various adsorption sites was similar for all pre-heating temperatures.

In conclusion, the salt loading dependence of the GSC retention volume on the salt-modified adsorbent could be established as linear functions for four different salt loading regions. The solute retention could be interpreted on the basis of a linear

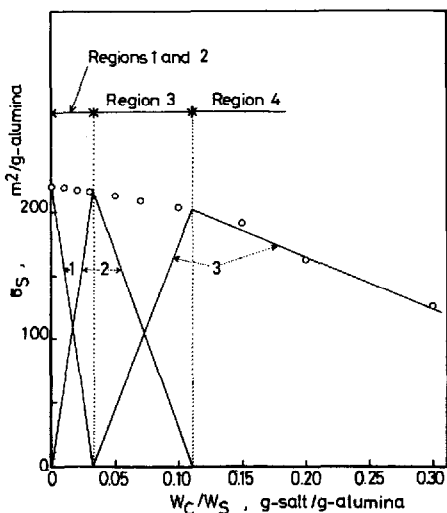


Fig. 5. Distribution of surfaces with salt loading for salt-modified alumina adsorbent pre-heated at 500°C. Surfaces: 1, original alumina surface; 2, deactivated surface (monolayer of potassium carbonate dispersed in the form of ions and/or ion-pairs); 3, surface layer of fine particles or thin crystalline films of potassium carbonate (crystalline layer).

TABLE VIII

SPECIFIC SURFACE AREAS (m^2/g alumina) AND THEIR RATIOS

Pre-heating temperature ($^{\circ}\text{C}$)	σ_s^0	σ_1	σ_2	σ_1/σ_s^0	σ_2/σ_s^0	σ_1/σ_2
500	221	67.6	153.4	0.31	0.69	0.44
700	182	42.0	140.0	0.23	0.77	0.30
900	146	42.0	104.0	0.29	0.71	0.40
1000	105	27.3	77.7	0.26	0.74	0.35

combination of concurrent contributions from adsorption equilibria on subsurfaces distributed on the base adsorbent. This approach can be expected to provide important information of the properties of GSC adsorbents, and subsequent development of GSC for analytical applications.

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