CHROM. 9533

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

MODIFICATION OF ALUMINA WITH ALKALI-METAL FLUORIDES

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(Received June 14th, 1976)

SUMMARY

Variations in the adsorptivity of alumina produced by coating with alkali-metal fluorides are dependent on the nature and the amount of the salt coated and on the thermal treatment before and after the coating. Similar adsorption behaviours are observed on LiF- and CsF- and on NaF- and KF-modified aluminas. These phenomena are discussed in terms of the extent of the reaction of the alumina with the salt. Differences in the adsorption behaviour of the coated alumina with respect to saturated and unsaturated hydrocarbons can be explained mainly by the interaction of the solute with the alkali-metal ion on the surface.

INTRODUCTION

There has been continued interest in the adsorbents used for gas–solid chromatography (GSC) with the aim of extending their utility in gas chromatography, and many advantages have resulted. The coating of various adsorbents with inorganic salts in order to modify the adsorptivity has been carried out by many workers and interesting results have been reported[1–23]. However, few workers have systematically studied the effects on the adsorptivity of pre-heating of the support, of the nature and amount of the salt coating and of post-heating of the salt-coated adsorbent. In previous papers[21,22] it has been reported that the adsorptivity of alumina varies with the nature and the amount of the salt coating and with post-heating. In the present paper the effects on the absorptivity of alumina of pre-heating of the support, of the nature and amount of alkali-metal fluoride coating and of post-heating are described as an extension of the procedure of treating alumina with potassium fluoride–hydrofluoric acid solution.

EXPERIMENTAL

Reagents

Commercial guaranteed reagent-grade lithium, sodium and potassium fluorides

were used without further purifications. Caesium fluoride was prepared from caesium carbonate and hydrofluoric acid and used after elimination of the free acid by evaporation to dryness. The organic solutes used were commercial materials of guaranteed reagent or extra pure grade.

Adsorbent

Alumina Neobead MS.C (60–80 mesh) (Mizusawa Industrial Chemicals, Tokyo, Japan), manufactured as a catalyst and support for catalysts was used for the preparation of the adsorbent. The alumina was pre-heated at 200–1100° for 2 h before coating with alkali-metal fluoride. Coating of the alumina with NaF, KF and CsF was performed by evaporation on a water-bath of 25 ml of each fluoride solution in a polyethylene beaker containing 10 g of alumina. Since the solubility of LiF is low, coating with this salt could not be achieved by the above method, and was made as follows. To 25 ml of a suspension containing the desired amount of LiF, 10 g of alumina were added and the mixture was allowed to stand with occasional stirring until the precipitate of the salt had disappeared. Even with this method, alumina pre-heated at >1000° could not be coated with LiF. Thermal treatment of salt-coated alumina was carried out by heating in a porcelain dish at the desired temperature for 2 h in an electric furnace. The thermally treated alumina was packed in a column after resieving.

Chromatography

A Hitachi Model 023 gas chromatograph equipped with a thermal conductivity detector and stainless-steel columns (100 cm × 0.3 cm I.D.) was used. The carrier gas (helium) flow-rate was 40 ml/min. The samples were injected by means of a 10-μl microsyringe. The column temperature was 80° for aliphatic hydrocarbons and 180° for aromatic hydrocarbons.

Each solute gave a symmetrical peak on the modified alumina, and the retention volume was measured from the air peak and the peak maximum; corrections were made for the water-vapour pressure at a soap flow-meter and for the pressure drop in the column. The specific surface area of the adsorbent was measured by adsorption of p-nitrophenol from benzene solution according to the method of Giles et al.[24].

RESULTS AND DISCUSSION

The adsorptivity of the modified alumina varied with pre-heating of the alumina before the coating with the salt, and the effect of pre-heating at 500–1100° was studied first with the adsorbent coated with 10% (w/w based on the free alumina) of NaF and with post-heating at 200–600°. As shown in Fig. 1, the specific retention volume, V_g, of ethylbenzene on NaF-modified alumina post-heated at 200–400° decreased with increasing pre-heating temperature, but the adsorbent post-heated at 600° showed a maximum in retention volume at a pre-heating temperature of 700°. The specific surface area, A_s, of these adsorbents decreased with increasing pre-heating temperature as shown in Fig. 2, but that of the adsorbent post-heated at low temperature increased with increasing pre-heating temperature above 900°. The adsorption constant, K_s, of ethylbenzene on these adsorbents, calculated from the relation $V_g = K_s A_s$, showed a maximum at a pre-heating temperature of 700° independent of the
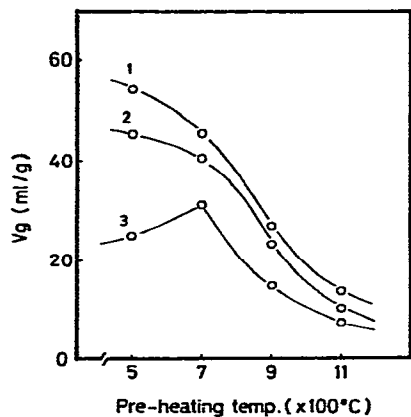
Fig. 1. Effect of the pre-heating temperature of the alumina on the retention of ethylbenzene on NaF (10%)-modified alumina. Column temperature: 180°. Post-heating temperature of the modified alumina: (1) 200°; (2) 400°; (3) 600°.
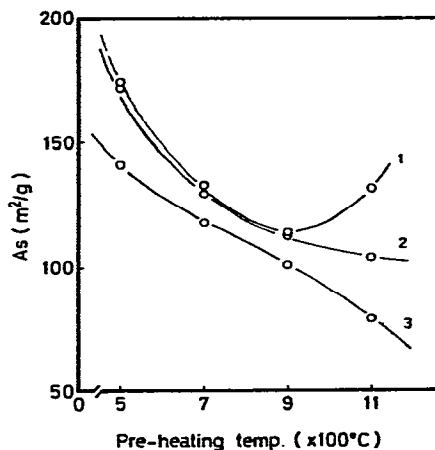
Fig. 2. Variation of the specific surface area of NaF-modified alumina with the pre-heating temperature of the alumina. Adsorbent as in Fig. 1.

post-heating temperature, and was low when the post-heating temperature was high as shown in Fig. 3. Similar variations in V_g and K_s for aliphatic hydrocarbons were observed at the column temperature of 80°.

The effect of the post-heating temperature was then studied for the adsorbent pre-heated at 700 and 1100° and coated with 10% of each salt. These pre-heating temperatures were selected so as to minimize the retention time. As shown in Fig. 4, the retention volume of ethylbenzene decreased with increasing post-heating temperature, except for the adsorbent pre-heated at 700° and coated with 10% of CsF which showed a maximum at a post-heating temperature of 600°. The A_s values of these adsorbents decreased with increasing post-heating temperature, except for the adsorbent pre-heated at 1100° and coated with 10% of CsF which showed a maximum at a post-heating temperature of 600°, but the variation differed according to the salt
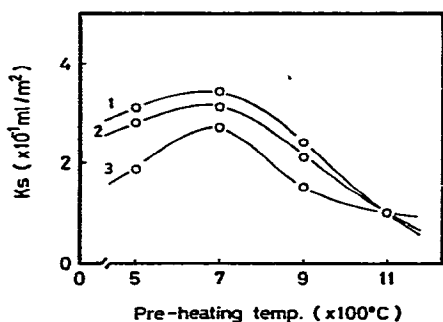

Fig. 3. Variation of the adsorption constant of ethylbenzene with pre-heating temperature on NaF-modified alumina at 180°. Adsorbent as in Fig. 1.
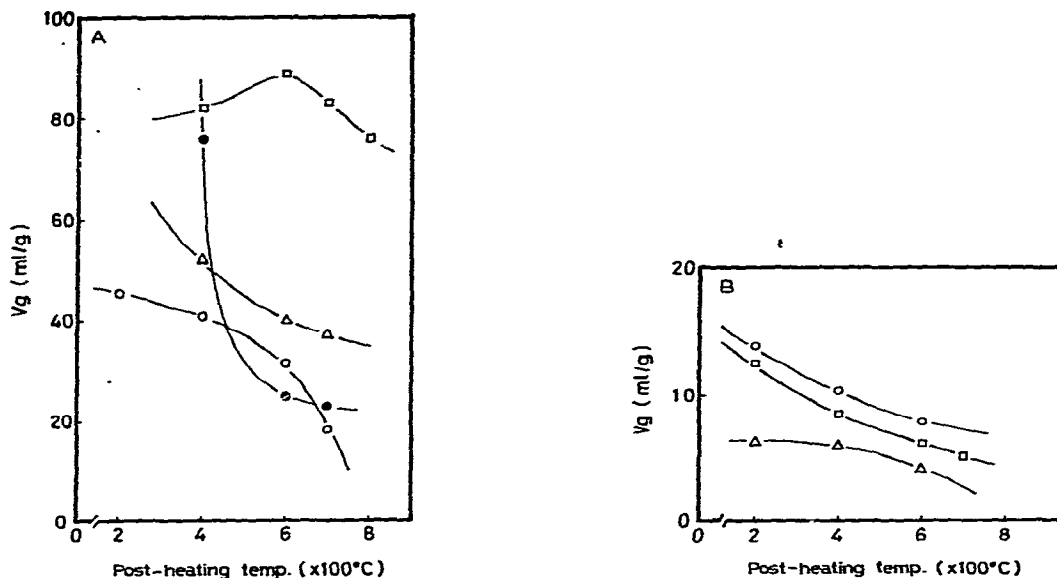
Fig. 4. Effect of the post-heating temperature of the modified alumina on the retention of ethyl-benzene. Pre-heating temperature of the alumina: (A) 700°; (B) 1100°. Column temperature: 180°. Salt coated (10%): ●, LiF; ○, NaF; △, KF; □, CsF.

coated (Fig. 5). The K_s values of ethylbenzene on these adsorbents varied with the post-heating temperature and the salt coated when the pre-heating temperature was low (700°) as shown in Fig. 6. When the alumina was pre-heated at 1100°, however, the value of K_s of ethylbenzene on the CsF-modified adsorbent slightly decreased with increasing post-heating temperature, and the K_s values obtained on NaF- and
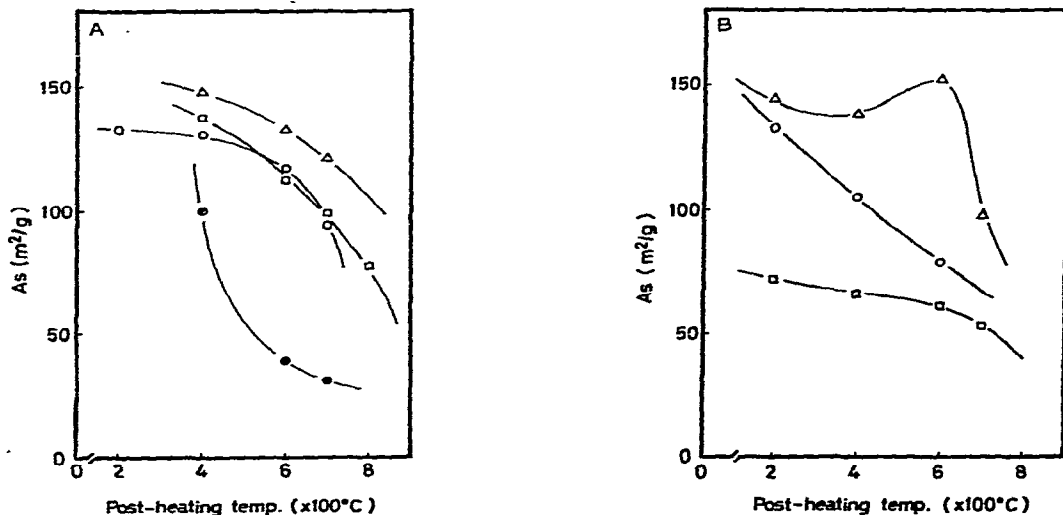

Fig. 5. Variation of the specific surface area of the modified alumina with post-heating temperature. Other details as in Fig. 4.
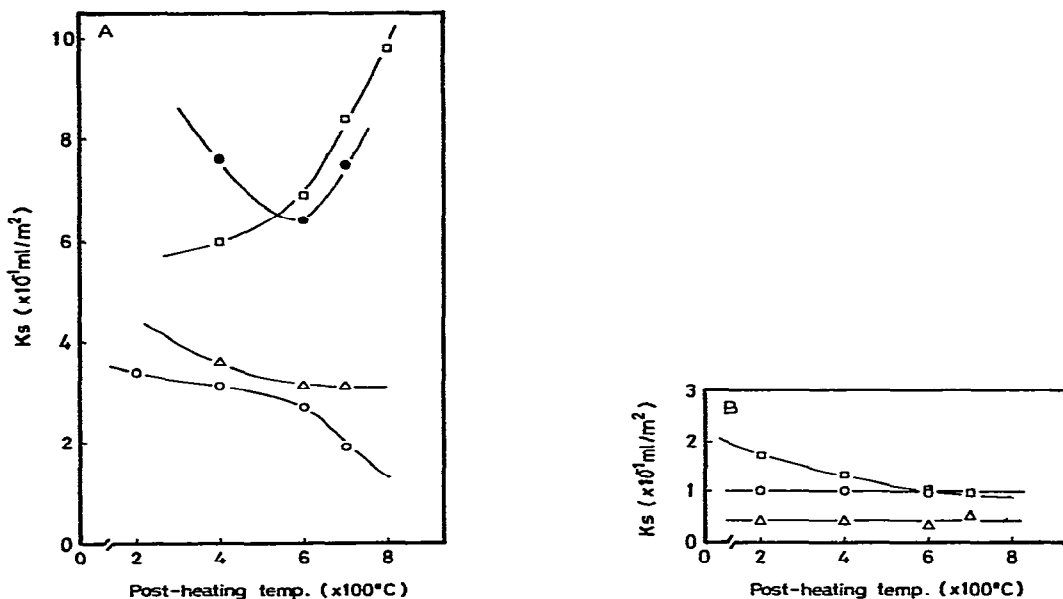
Fig. 6. Variation of the adsorption constant of ethylbenzene with post-heating temperature on modified alumina at 180°. Other details as in Fig. 4.

KF-modified adsorbents were constant, independent of the post-heating temperature. The values of K_s were lower than those obtained on the adsorbent pre-heated at 700°. The variations in the values of V_g of ethylbenzene with the post-heating temperature on the adsorbents pre-heated at 1100° and modified with NaF and KF, and on the other adsorbents, are believed to be caused by the variation of A_s of the adsorbent only and by both A_s and K_s respectively.

The reason for the variations in the value of K_s shown in Fig. 6 is considered to be as follows. From Table I, it can be seen that the melting point of CsF is much lower than those of other salts, and the melting points of Li_3AlF_6 and Cs_3AlF_6, considered to be formed in the following reaction, are lower than those of the corresponding sodium and potassium salts.

$$6\ MF + 2\ Al_2O_3 \rightarrow 3\ MAlO_2 + M_3AlF_6$$
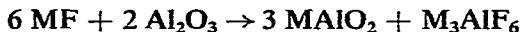
On LiF- and CsF-coated alumina surfaces the extent of the above reaction is believed to increase with increasing post-heating temperature, and therefore the chemical

TABLE I

MELTING POINTS OF ALKALI-METAL FLUORIDES AND HEXAFLUOROALUMI-NATES[25]

Salt	M.p. (°C)	Salt	M.p. (°C)
LiF	848	Li_3AlF_6	800
NaF	995	Na_3AlF_6	1009
KF	856	K_3AlF_6	1030
CsF	682	Cs_3AlF_6	723

and physical properties of the surface vary continuously. On NaF- and KF-modified surfaces, however, the above reaction is thought to proceed with difficulty as the melting points of each fluoride and reaction product are high, and the regular crystal of each fluoride is produced. Similarities in the adsorption behaviours of ethylbenzene on LiF- and CsF-modified adsorbents and on NaF- and KF-modified adsorbents, as shown in Fig. 6B, can be explained by these considerations. On the other hand the K_s value of ethylbenzene on the CsF-modified adsorbent pre-heated at 1100° decreased gradually with increasing post-heating temperature and tended to a constant value. This behaviour is similar to those exhibited by the NaF- and KF-modified adsorbents as shown in Fig. 6B. Values of K_s of ethylbenzene obtained on NaF- and KF-modified aluminas pre-heated at 1100° were constant. From these results it is suggested that the reaction of the alumina with the salt proceeds with difficulty with increasing pre-heating temperature as dehydration and crystallization of the alumina are promoted and the homogeneous layer of the fluoride is formed.

The effect of the amount of the salt coated was studied with pre-heating at 700° and post-heating at 600° respectively. These conditions were selected so as to obtain good separations of solutes in a short time. Fig. 7 shows that V_g of toluene decreased with increasing amount of the salt coated, and this tendency varied according to the salt coated. As shown in Fig. 8, the A_s values of the adsorbent increased with increasing amount of NaF, KF and CsF coated, but decreased with the amount of LiF coated. The value of K_s decreased with increasing amount of the salt coated and tended to a constant value as shown in Fig. 9. From these results it is suggested that
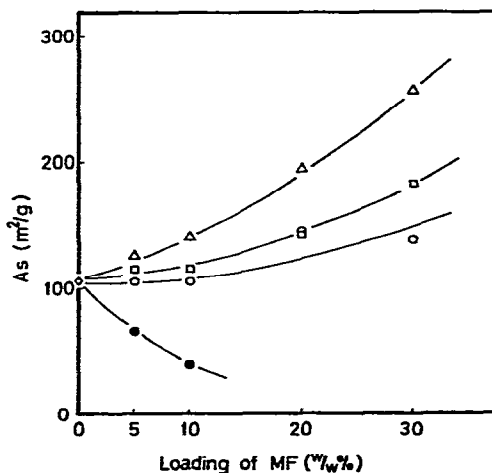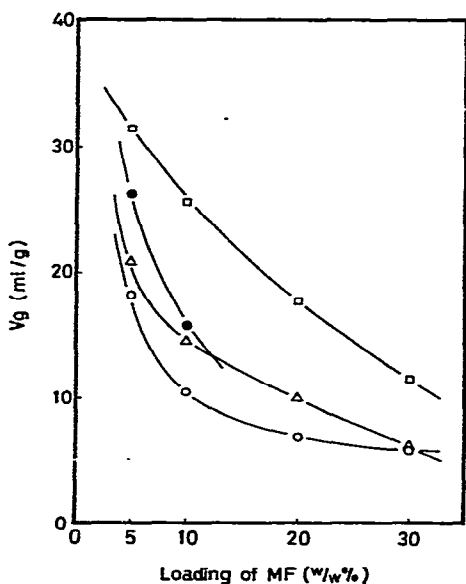

Fig. 7. Effect of the amount of salt coated on the alumina on the retention of toluene. Pre-heating temperature of the alumina: 700°. Post-heating temperature: 600°. Column temperature: 180°. Salts: ●, LiF; ○, NaF; △, KF; □, CsF.

Fig. 8. Variation of the specific surface area with the amount of the salt coated on the alumina. Adsorbent as in Fig. 7.
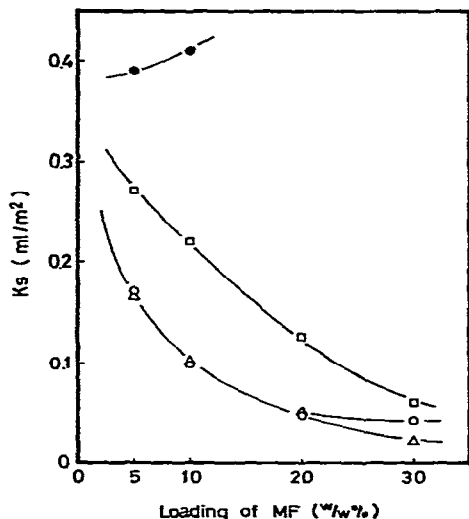
Fig. 9. Variation of the adsorption constant of toluene at 180° on modified alumina with the amount of the salt coated. Adsorbent as in Fig. 7.
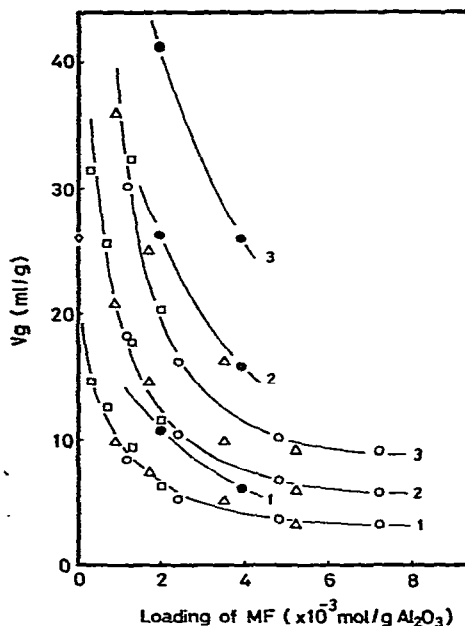
Fig. 10. Effect of the amount of the salt coated (moles per gram of the alumina) on the retention of benzene and its alkyl derivatives. Column temperature: 180°. Solutes: 1 = benzene; 2 = toluene; 3 = ethylbenzene. Adsorbent as in Fig. 7.

the adsorptive properties of these adsorbents with respect to p-nitrophenol and hydrocarbon solutes are different.

In Figs. 7–9 weight percentage is used conventionally to show the amount of the salt coated. It is more appropriate to show the amount (in moles) of the salt coated per gram of alumina (corresponding to the moles of salt per unit surface area of alumina) since the modification of the adsorptivity of the surface by reaction and the blocking of active adsorption sites are considered to be directly related to the amount of coating. In Fig. 10 the V_g of the solute is plotted against the moles of salt coated per gram of alumina. It can be seen that the variation in V_g with increasing amount of the salt coated is independent of the nature of the salt. The variation in A_s of the adsorbent with the amount of the salt coated differed according to the nature of the salt as shown in Fig. 11. Therefore the value of K_s is different for each salt coated but the variation in K_s with the amount of salt coated is similar for each salt as shown in Fig. 12.

The values of K_s for aliphatic hydrocarbon solutes on the modified alumina decreased in the order LiF > CsF > KF > NaF, but the differences in K_s became small with increasing amount of the salt coated. When the amount of salt coated was high the difference between the K_s values of each salt coated was small, and therefore the non-specific interactions between the solute molecule and the surface seem to be largely unaffected by the nature of the metal ion. However, as shown in Fig. 13, the ratio of the V_g values of saturated aliphatic hydrocarbons to those of n-pentane
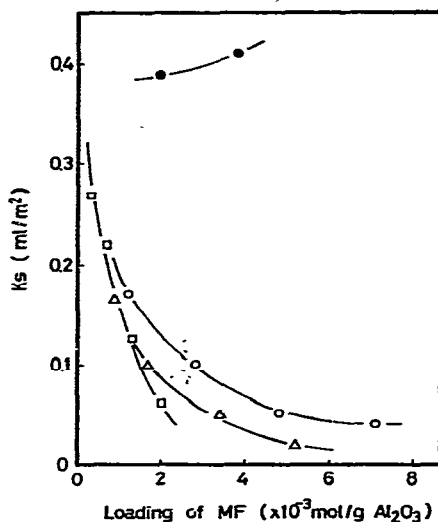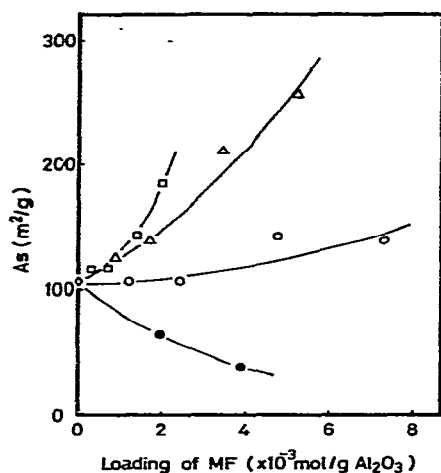
Fig. 11. Variation of the specific surface area of modified alumina with the amount of the salt coated (moles per gram of alumina). Adsorbent as in Fig. 7.

Fig. 12. Variation of the adsorption constant of toluene at 180° with the amount of the salt coated (moles per gram of alumina). Adsorbent as in Fig. 7.

decreased in the order CsF > KF > NaF, and increased with increasing number of carbon atoms possessed by the solute. Therefore the non-specific interactions between saturated aliphatic hydrocarbons and alkali-metal ions are thought to increase with increasing ionic radius of the metal ion[26] and with the number of carbon atoms of the solute. When the amount of salt coated is low the composition of the surface layer is believed to vary considerably with the salt coated due to the different extents of the reaction shown above. Differences between the K_s values of each salt in this coating range are considered to be based on this variation.

The values of K_s for benzene, alkylbenzene and unsaturated aliphatic hydro-carbons decreased in the order LiF > NaF > KF > CsF. As shown in Fig. 13B, the ratio of V_g of 1-hexene to that of n-hexane decreased in the same order. These results suggest that the specific interaction between the π-electrons of an unsaturated solute and an alkali-metal ion is the main factor in the retention of the unsaturated solute. As shown in Fig. 13C, the ratios of the V_g values of toluene and benzene and of ethylbenzene and benzene were independent of the salt coated, but the ratio of the values of propylbenzene and benzene increased in the order CsF > KF > NaF. Therefore factors due to the side chain must also be considered in the retention of an alkylbenzene possessing a large alkyl group. As shown in Fig. 14, the ratio of the V_g values of cis- and trans-2-hexene decreased with increasing amount of the salt coated and tended to a constant value except for the LiF-modified adsorbent. The value of this ratio decreased in the order LiF > NaF > KF > CsF, i.e., the same as that of the interaction of the π-electrons of the solute with the metal ion.

In this study the adsorbent modified with LiF was found to show irregular behaviour compared to the other adsorbents. This may be due to departure of the properties of Li+ from the trends shown by the remaining alkali metals. The alumina
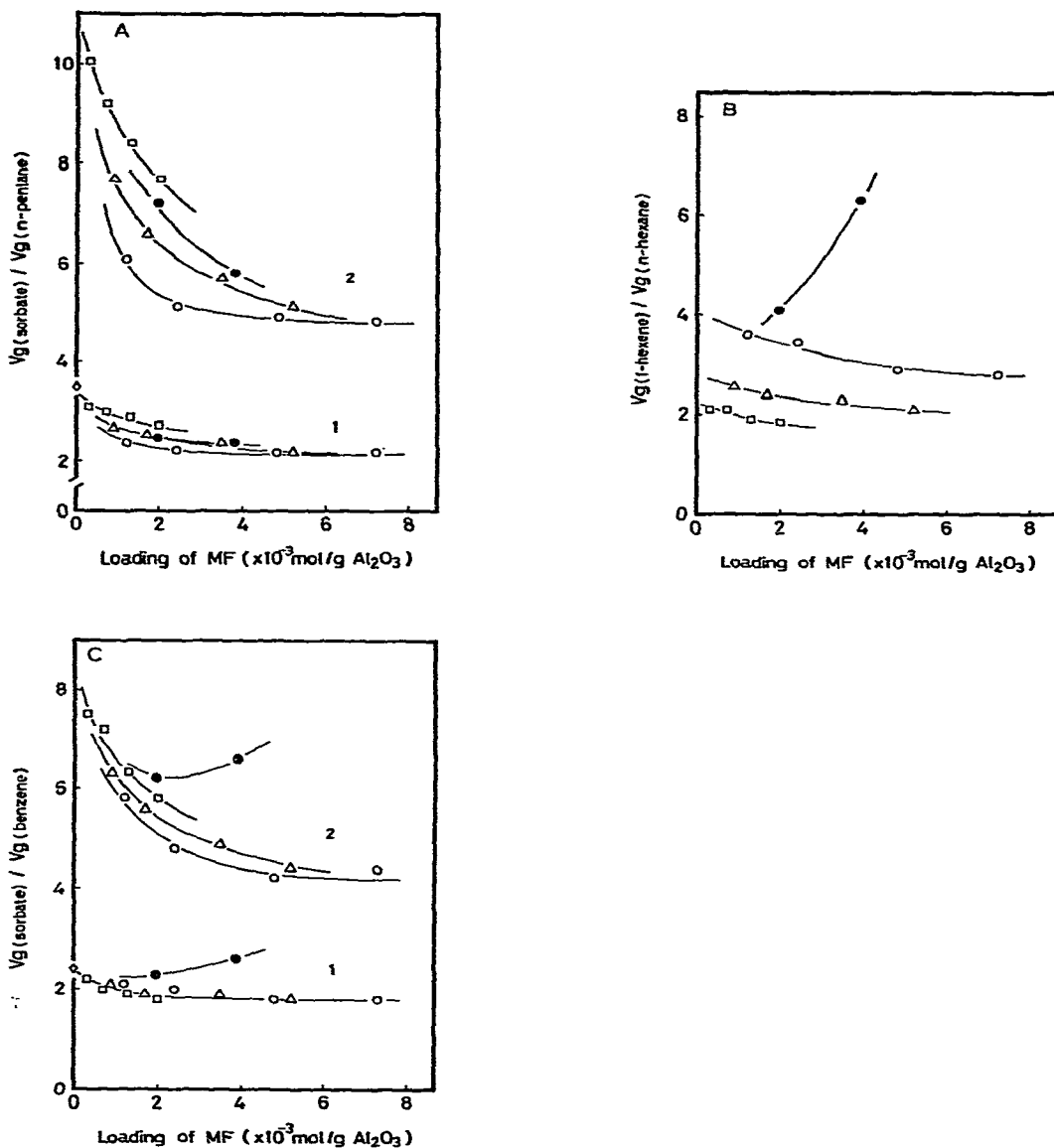
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Fig. 13. Variation of the ratio of the retention volumes with the amount of the salt coated. Solutes: (A) 1 = n-hexane, 2 = n-heptane; (C) 1 = toluene, 2 = n-propylbenzene. Column temperatures: (A) and (B), 80°; (C), 180°. Adsorbent as in Fig. 7.

modified with KF showed a high adsorptivity and only small variation in adsorptivity with post-heating compared to alumina treated with KF–HF solution[22]. These findings are believed to be due to the co-existence of $KAlO_2$ formed by the reaction of alumina with KF at the surface.
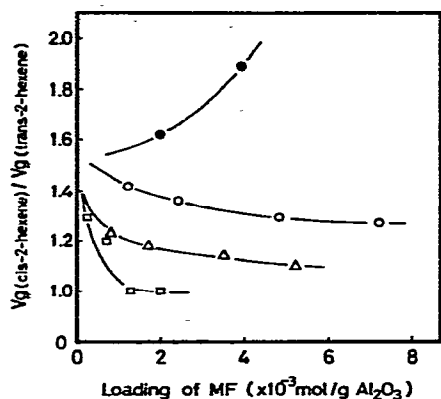
Fig. 14. Variation of the ratio of the retention volumes of *cis*- and *trans*-2-hexene with the amount of the salt coated. Adsorbent as in Fig. 7.

CONCLUSIONS

Modifications to the adsorptivity of alumina on coating with alkali-metal fluorides are dependent on the nature and amount of the salt coated and on the thermal treatment before and after the coating. These variations are thought to be due to the different extents of the reaction of alumina with the salt coated at the surface. The adsorption behaviours of these adsorbents with respect to saturated and unsaturated hydrocarbons can be explained mainly by non-specific and specific interactions of the solute with the alkali-metal ions. Suitable adsorbents for the separation of a given sample can thus be devised which give good separations of hydrocarbon solutes possessing high boiling points and of *cis* and *trans* isomers.

ACKNOWLEDGEMENT

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