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EFFECT OF ADSORPTION OF CARRIER GAS IN GAS–SOLID CHROMATOGRAPHY

THEORY AND ITS APPLICATION TO THE SEPARATION OF HYDROGEN ISOTOPES

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SUMMARY

Analytical formulae to express the effect of adsorption of carrier gas in gas–solid chromatography have been derived from the theory of non-linear ideal chromatography and the Langmuir adsorption theory. They predict improvement of symmetry in peak shape, reduction in retention volume, independence of relative retention on the kind of carrier gas used, and the smaller dependence of retention volume on column temperature when an inert gas is replaced with an adsorptive gas as carrier. The formulae were satisfactorily applied to explain experimental results on the separation of hydrogen isotopes by a series of ammonia-treated molecular sieve 13X columns.

INTRODUCTION

The use of carbon dioxide[1], water vapor[2], ammonia[3] and hydrogen[4] as carrier gases for gas chromatography (GC) has been demonstrated, to shorten the elution time and improve the symmetry of the peak, leading to a more efficient separation of materials. OHKOSHI, one of the authors of this paper, has found that the use of hydrogen as a carrier gas has a remarkable effect on the GC separation of HD and D_2 by an activated molecular sieve column[4]: HD and D_2, which are not eluted in several hours when helium is used as carrier gas, are eluted within several minutes as fully separated symmetrical peaks with hydrogen carrier gas. In the present work, analytical formulae derived from the theory of chromatography and the Langmuir adsorption theory, gave a satisfactory explanation for the experimental results obtained, for the separation of hydrogen isotopes by a series of molecular sieve columns whose adsorption capacities for hydrogen were finely controlled by pretreatment with ammonia. Ammonia was chosen because the amount used can be readily determined by a conventional gas volumetric method and also it is less chemically reactive than water vapor with respect to the molecular sieve[5], although both the vapors may be used for the present experiment.

General theory

The theory of non-linear ideal chromatography for a single solute i (refs. 6–8) gives the relation between the adjusted retention volume (retention volume minus hold-up volume) V_i (ml) and the amount of specific adsorption of the solute $f(p_i)$ (mmole/g),

$$V_i = m[\partial f(p_i)/\partial c_i]_T = m[\partial f(p_i)/\partial p_i]_T(\partial p_i/\partial c_i)_T \qquad (1)$$

where m is the total weight (g) of an adsorbent in the column, T the column temperature (°K) and p_i and c_i the equilibrium pressure and concentration of the solute in gas phase at column outlet (atm and mmole/ml), respectively.

If $f(p_i)$ can be assumed to be of the Langmuir type, we obtain

$$f^{\mathrm{in}}(p_i) = v_m b_i p_i/(1 + b_i p_i) \qquad (2)$$

for an inert carrier gas, and

$$f^{\mathrm{ad}}(p_i) = v_m b_i p_i/(1 + b_i p_i + b_{\mathrm{ad}} p_{\mathrm{ad}}) \qquad (3)$$

for an adsorptive carrier gas, where v_m is the monolayer adsorption amount of i assumed to be the same as that of the carrier gas[9], and b the Langmuir constant. It should be pointed out that eqn. 3 is in a form for mixed solutes, but $f^{\mathrm{ad}}(p_i)$ can be considered as a function of p_i only, since p_{ad} is kept at an almost constant value of 1 atm throughout the experiments.

Eqns. 1, 2 and 3 and the relation $p_i = c_i RT$ give

$$V_i^{\mathrm{in}} = mRTv_m b_i/(1 + b_i p_i) \qquad (4)$$

and

$$V_i^{\mathrm{ad}} = mRTv_m b_i/(1 + b_i p_i + b_{\mathrm{ad}} p_{\mathrm{ad}}) \qquad (5)$$

under the conditions that $b_i p_i/(1 + b_i p_i) \leqslant 1$ and $b_i p_i/(1 + b_i p_i + p_{\mathrm{ad}} p_{\mathrm{ad}}) \leqslant 1$, because of the small p_i value.

Now we apply the equations to the present system. In the present work, helium was used as an inert carrier gas, and light hydrogen as an adsorptive carrier gas. If the ammonia adsorption, as described later, simply gives rise to the decrease of the surface area available for hydrogen adsorption, we have

$$v_m = kv_{\mathrm{NH_3}}(1 - \theta_{\mathrm{NH_3}}) \qquad (6)$$

where $v_{\mathrm{NH_3}}$ and $\theta_{\mathrm{NH_3}}$ are the monolayer adsorption amount and the coverage of ammonia and k is a proportionality constant. From eqns. 4, 5 and 6 we obtain

$$V_i^{\mathrm{He}} = kv_{\mathrm{NH_3}}(1 - \theta_{\mathrm{NH_3}})mRTb_i/(1 + b_i p_i) \qquad (7)$$
$$(i = \mathrm{H_2, HD\ or\ D_2})$$

and

$$V_i^{\mathrm{H_2}} = kv_{\mathrm{NH_3}}(1 - \theta_{\mathrm{NH_3}})mRTb_i/(1 + b_i p_i + b_{\mathrm{H_2}} p_{\mathrm{H_2}}) \qquad (8)$$
$$(i = \mathrm{HD\ or\ D_2})$$

EXPERIMENTAL

Apparatus and gas chromatographic procedure

A conventional all glass apparatus with high vacuum line was used for measuring the adsorption isotherms of hydrogen isotopes on a commercial molecular sieve 13X at −195° and −183°, and also for treating a column with a known amount of ammonia. A Shimazu Model 1B-2 gas chromatograph equipped with a thermal conductivity detector was used for recording gas chromatograms. The separatory column (4 mm I.D. × 40 cm) was the molecular sieve 13X (60–80 mesh) packed in U-glass tubing with a stop cock and a reflux cock, as shown in Fig. 1. After treatment with ammonia, the column was connected to the gas chromatograph with silicon rubber tubing, and air in part A (*cf.* Fig. 1) of the glass tubing was replaced by a carrier gas, before the gas was introduced into the column. Flow rates of helium and hydrogen carrier gas were kept at 200 and 100 ml/min, respectively, throughout the experiments. The difference between the pressures at inlet and outlet of the column was so small (not more than 5 cm Hg) that the pressure correction for the retention volume was neglected. A glass made gas sample injection device connected to the vacuum line was used to introduce a known amount of sample gas under reduced pressure into the column. p_i was calculated according to the method by CREMER AND HUBER[10].

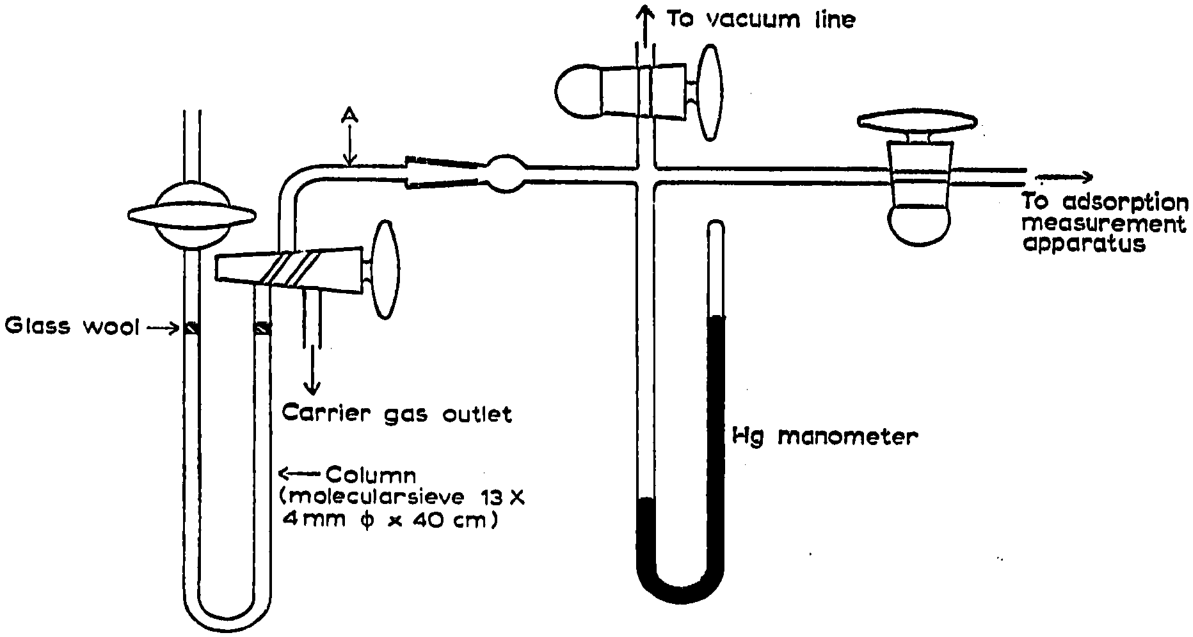

Fig. 1. Column preparation.

Materials

The helium carrier gas was purified by passing it through an activated carbon trap cooled at —195°. Pressurized ultra-pure dry hydrogen generated by "Elhygen" hydrogen generator with maximum capacity of 150 ml/min (Milton Roy Co., U.S.A.) was also used as a carrier gas. Deuterium of 99.9 % purity (Showa Denko Co. Ltd.) was used without further purification. A mixture of H_2, HD and D_2 gases was made by the reaction of H_2 and D_2 in the molar ratio 1 to 1.70 in the presence of a platinum net catalyst heated at 300°C, overnight in a side tube of a 3-l glass bulb. Its composition was determined by GC[11]. Commercial ammonia from a cylinder was purified by bringing it into contact in the liquid state with sodium metal and then distilling it into an evacuated glass bulb. Nitrogen of 99.99 % purity was used for the determination of surface area without further purification.

Preparation of the ammonia-treated column

The molecular sieve column was first activated at 300°C in a stream of hydrogen for 1 h, connected to a high vacuum line and then evacuated (*cf.* Fig. 1). An amount of ammonia corresponding to the nitrogen monolayer adsorption amount (179 ml (s.t.p.)/g) was then introduced to the column at room temperature. After the efficiency of the column had been tested at —195° and —183°C, it was again connected to the vacuum line, evacuated at dry ice temperature to remove adsorbed hydrogen and heated to a higher temperature to remove a known amount of ammonia. Repetition of this procedure enabled us to make a series of columns with different ammonia coverage.

Stringent precautions were taken to obtain a uniform coverage of ammonia throughout the column: *e.g.* after a definite amount of ammonia was introduced or removed, the column was immersed, for example, in hot water in a Dewar vessel whose temperature was adjusted so that an equilibrium pressure of ammonia of at least several centimeters was achieved. The column was then allowed to cool down in the Dewar vessel. The amount of ammonia remaining in gas phase in the column at room temperature was generally negligible except in the case of the preparation of some columns with high ammonia coverage. Such a column preparation enabled us to obtain quite reproducible data.

RESULTS AND DISCUSSION

Adsorption experiment

The adsorption of H_2 and D_2 at —195° and —183°C was measured on a molecular sieve 13X sample activated at 300°C and also on the sample which had first been modified by the ammonia treatment within a θ_{NH_3} range between 0.3 and 0.5, where θ_{NH_3} was temporarily defined as the ratio of the adsorption amount of ammonia to the monolayer adsorption amount of nitrogen. As seen in Fig. 2, Freundlich

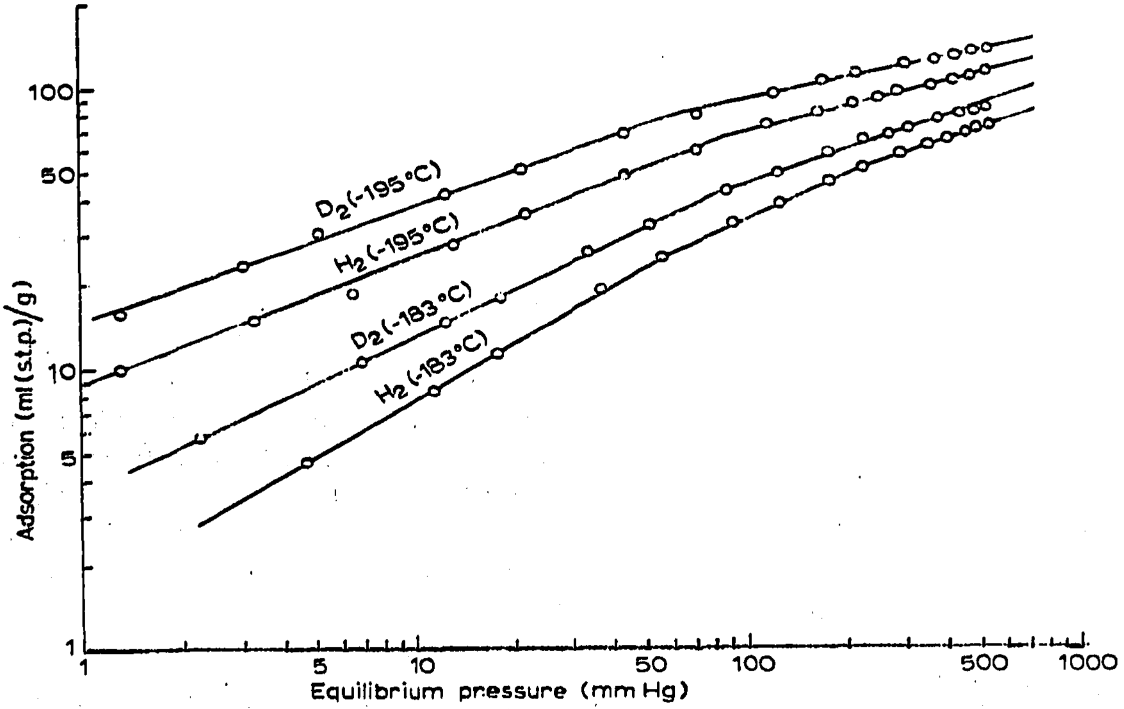

Fig. 2. Adsorption isotherms of H_2 and D_2 on an activated molecular sieve 13X at − 183° and − 195° C.

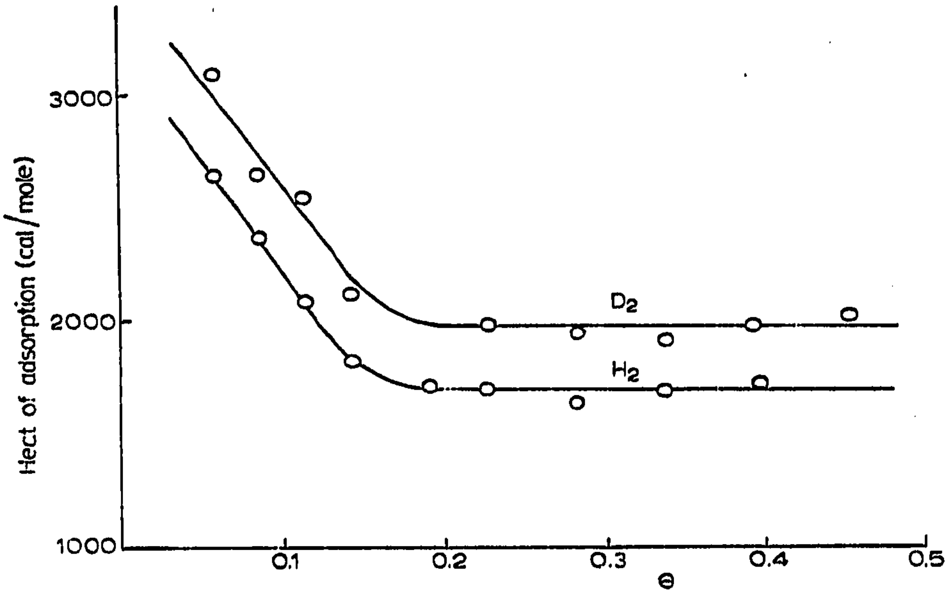

Fig. 3. Isosteric heat curves of H_2 and D_2. Sample: the same as in Fig. 2.

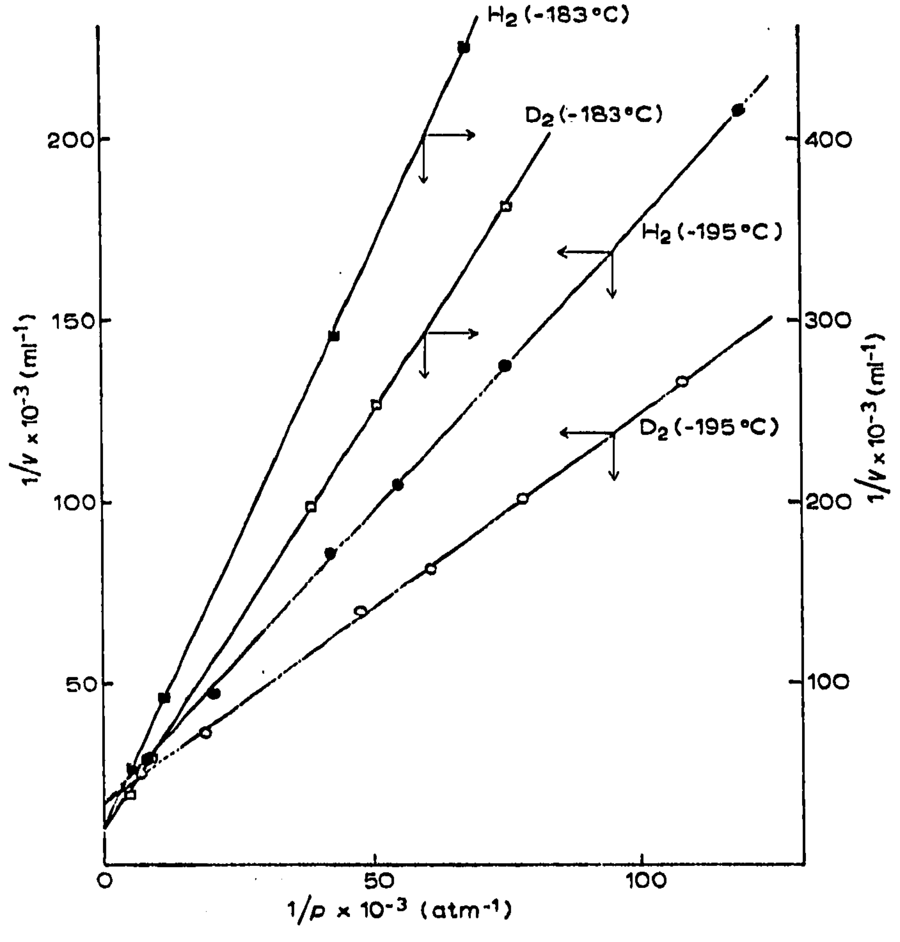

Fig. 4. The Langmuir plot for H_2 and D_2 adsorption on an ammonia-treated molecular sieve 13X sample at − 183° and − 195°C. θ_{NH_3}: 0.497.

adsorption isotherms were obtained for the activated sample, isosteric heat of adsorption Q hence depending on θ_{H_2} and θ_{D_2} (see Fig. 3). In the case of a modified sample, typical Langmuir isotherms were observed, as shown in Fig. 4, giving a constant isosteric heat, as shown in Table I.

These facts show that the ammonia treatment produced a homogeneous surface from a heterogeneous one for hydrogen adsorption. It should be pointed out, however, that the heat of adsorption of the modified sample is smaller than that of

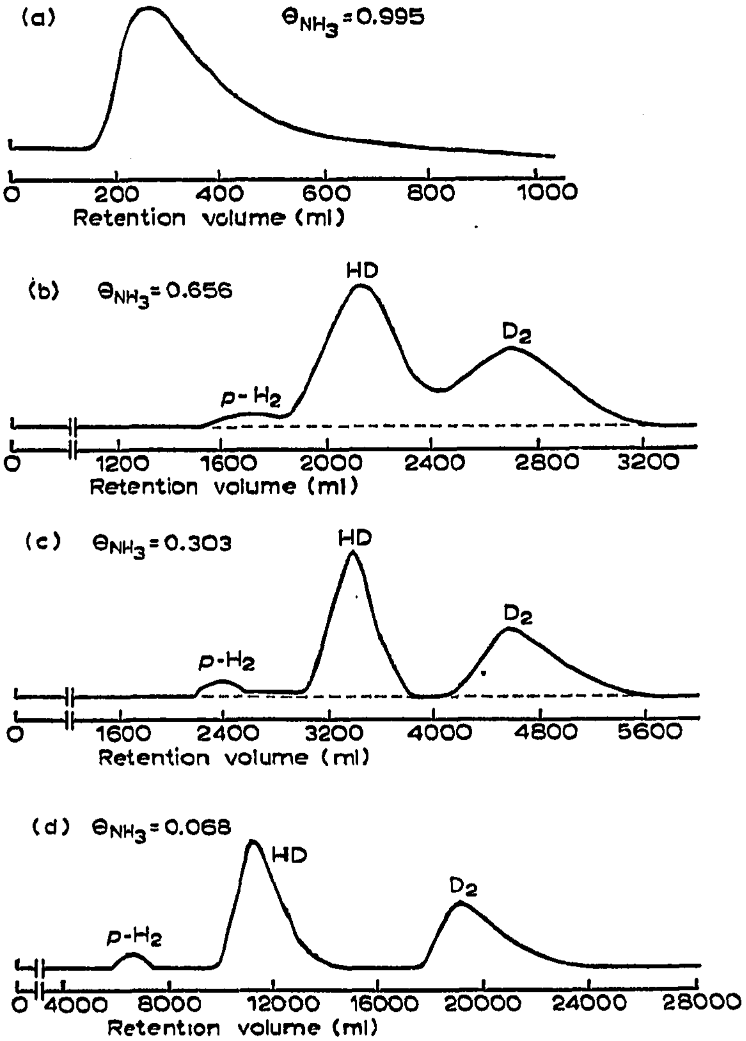

Fig. 5. Gas chromatograms of hydrogen isotopes with helium carrier gas. Helium flow rate: 200 ml/min. Column temperature: −195°C. Hold-up volume: 100 ml. H_2:HD:D_2 = 14.8:44.4:40.8. Sample size: (a) 0.149, (b) 0.238, (c) 0.577 and (d) 1.221 ml s.t.p.

TABLE I

HEAT OF ADSORPTION FOR AMMONIA-TREATED SAMPLE

Method	θ_{NH_3}	Q_{H_2} *(cal)*	Q_{D_2} *(cal)*	$Q_{D_2} - Q_{H_2}$ *(cal)*
Adsorption	0.497	−1010	−1450	−440
Gas chromatography	0.3 ~ 1.0	−1030	−1580	−550

the activated sample within the whole range of the observed hydrogen coverage. This means that the ammonia adsorption exerts its effects not only by decreasing the surface area available for hydrogen adsorption, but also by modifying the quality of the adsorbent.

Gas chromatograms

Fig. 5 illustrates the chromatograms of H_2, HD and D_2 mixtures as a function of θ_{NH_3} with helium as a carrier gas. As seen in Fig. 5(a) and Fig. 9, a sample pulse was poorly retained by the column, when θ_{NH_3} was almost equal to 1. As ammonia was removed, three peaks were developed, which were identified as p-H_2, a mixture of HD and o-H_2 and D_2 by a comparison of the chromatograms with those of H_2 and D_2 alone (see Fig. 6). At a low ammonia coverage (less than 0.3), a plateau appeared between the p-H_2 and the o-H_2 peak. This was found to be due to a transient separation of p-H_2 produced by the catalytic conversion of o-H_2 over a paramagnetic impurity* in the molecular sieve during the course of the elution.

Fig. 7 illustrates the chromatograms with hydrogen as carrier gas. Peaks of HD and D_2 were quite symmetrical in shape. Partial separation of o-D_2 and p-D_2 was observed only for active columns.

Effect of sample size

Since $b_{H_2} \approx b_{D_2}$ and $p_{H_2} \gg p_{D_2}$ in eqn. 8, it may be expected that in practice $V_{D_2}^{H_2}$ does not depend on p_{D_2}, and hence does not depend on the sample size of D_2. In such a case, the peak will be almost symmetrical in shape as expected from the theory of chromatography. On the other hand, $V_{D_2}^{He}$ directly depends on p_{D_2}, as

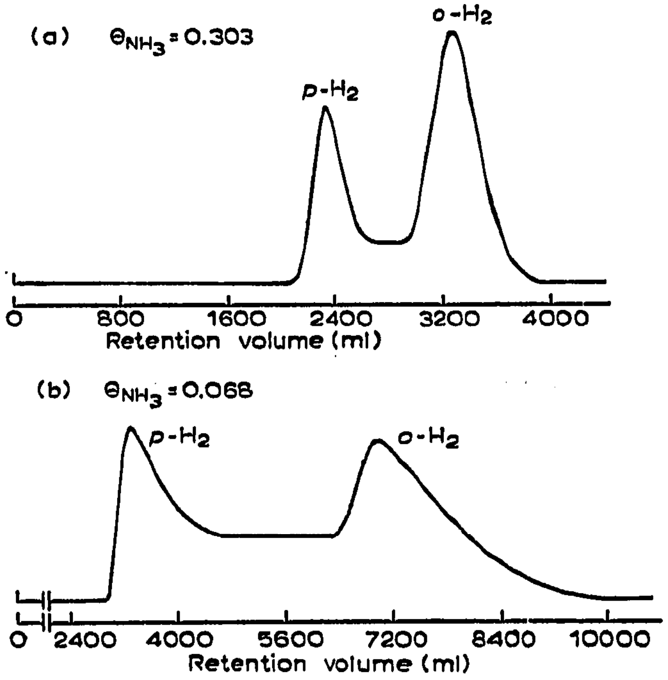

Fig. 6. Gas chromatograms of light hydrogen with helium carrier gas. Sample size: (a) 0.968 and (b) 2.243 ml s.t.p. Column conditions: the same as in Fig. 5.

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* Iron as an impurity was detected by X-ray fluorescence analysis.

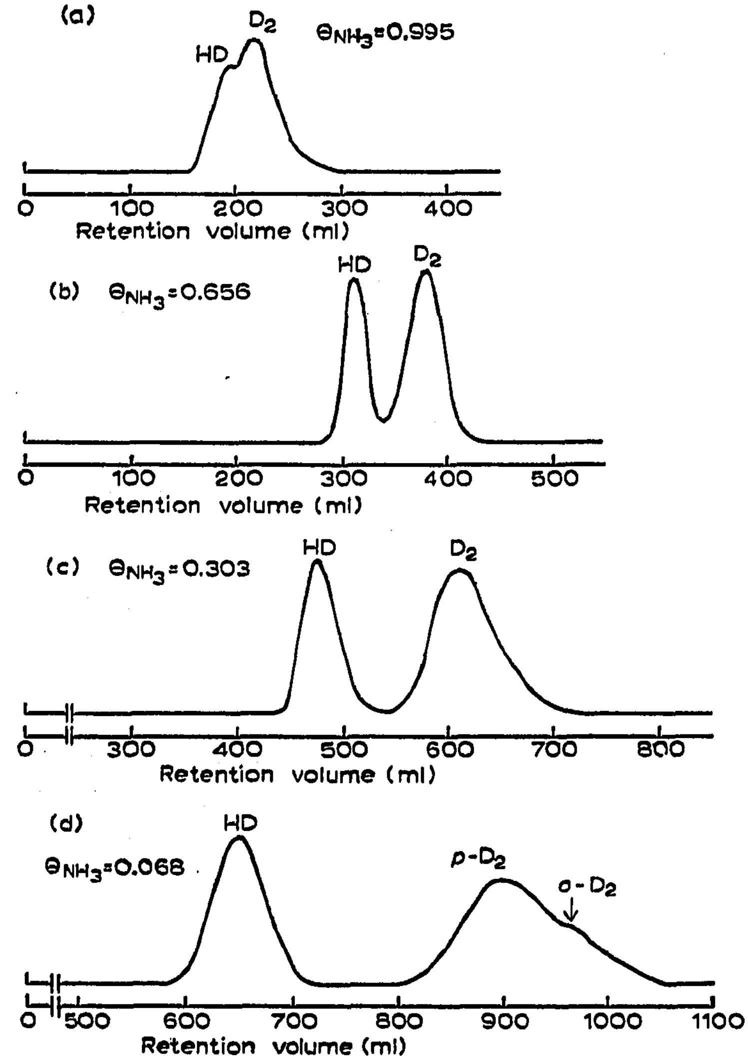

Fig. 7. Gas chromatograms of hydrogen isotopes with hydrogen carrier gas. Hydrogen flow rate: 100 ml/min. Sample size: (1) 0.149, (2) 0.238, (3) 0.492 and (4) 0.439 ml s.t.p. Other conditions: the same as in Fig. 5.

indicated by eqn. 7. The peak will thus be unsymmetric in shape as in a usual case of gas–solid chromatography (GSC). These predictions were confirmed experimentally at the column temperatures of −195° and −183°C. A typical example is shown in Fig. 8. It should be emphasized in this figure that with hydrogen as carrier gas the peaks are still symmetric in shape in spite of their having much higher p_i values than peaks obtained with helium.

The relation between $V_{0,i}$ and $\theta_{\mathrm{NH_3}}$

From eqns. 7 and 8, we obtain $V_{0,i}$, the adjusted retention volume of i at zero sample size (*i.e.* $p_i = 0$),

$$V_{0,i}^{\mathrm{He}} = kv_{\mathrm{NH_3}}(1 - \theta_{\mathrm{NH_3}})mRTb_i \tag{9}$$

and

$$V_{0,i}^{\mathrm{H_2}} = kv_{\mathrm{NH_3}}(1 - \theta_{\mathrm{NH_3}})mRTb_i/(1 + b_{\mathrm{H_2}}p_{\mathrm{H_2}}) \tag{10}$$

Hence

$$V^{He}_{0,i}/V^{H_2}_{0,i} = 1 + b_{H_2}p_{H_2} \tag{11}$$

It will be thus expected that both $V^{He}_{0,i}$ and $V^{H_2}_{0,i}$ decrease linearly with the increase of θ_{NH_3} under given column conditions. Furthermore, since $b_{H_2} > 0$ and p_{H_2} = constant = 1 atm, eqn. 11 suggests that $V^{He}_{0,i}$ is essentially bigger than $V^{H_2}_{0,i}$, their ratio being independent of the ammonia treatment, and that the Langmuir constant for hydrogen as carrier gas can be determined from the data on the retention volume. The experimental results for D_2 at the column temperature of −195°C are shown in Fig. 9 and Table II. V_{0,D_2} values were determined by a linear extrapolation illustrated in Fig. 8. The linear relation between V_{0,D_2} and θ_{NH_3} was strictly observed within a θ_{NH_3} range between 0.3 and 1.0 and the calculated value of b_{H_2} was in good agreement with that from the adsorption data, as seen in Table II.

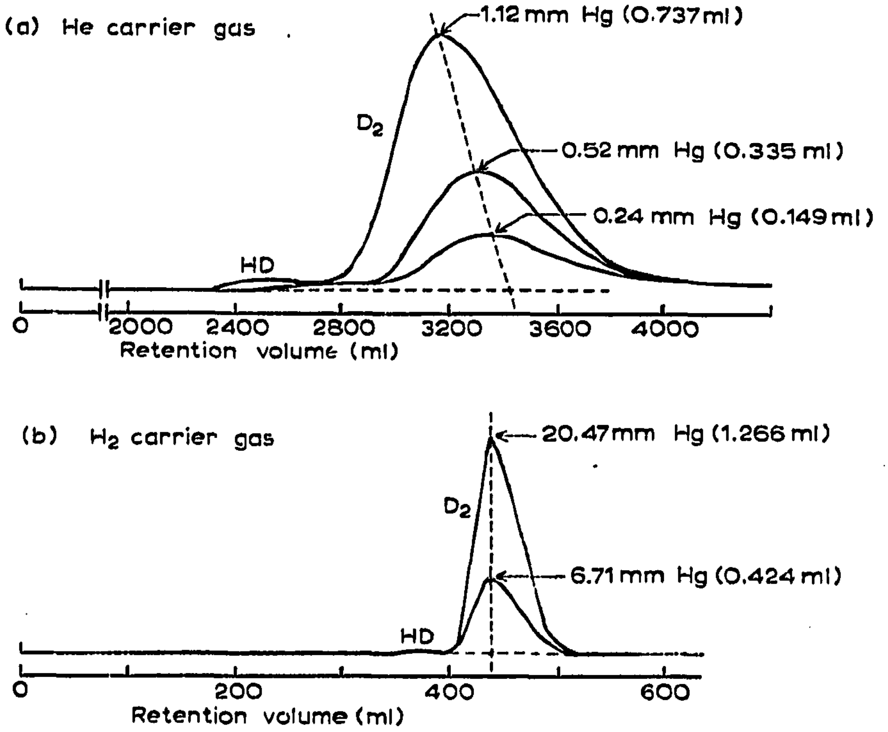

Fig. 8. Effect of sample size on the retention volume and the peak shape. Column temperature: − 195°C. θ_{NH_3}: 0.540. Sample gas: D_2.

The separation factor of hydrogen isotopes

One of the most important parameters associated with separation of materials is the separation factor, which is defined for two solutes *i* and *j* as

$$\alpha_{ij} = (c^s_i/c^g_i)/(c^s_j/c^g_j) = [f(p_i)/p_i]/[f(p_j)/p_j] \tag{12}$$

where *s* and *g* refer to the surface and the gas phase, respectively. Eqns. 2, 3, 9, 10 and 12 can be combined to give the separation factor at zero sample size

$$\alpha_{0,ij} = V^{He}_{0,i}/V^{He}_{0,j} = V^{H_2}_{0,i}/V^{H_2}_{0,j} = b_i/b_j = f(T) \neq f(\theta_{NH_3}) \tag{13}$$

That is to say, $\alpha_{o,ij}$ is simply equal to the relative retention of i to j and it depends on the column temperature, but not on the ammonia coverage. It should be specially emphasized that $\alpha_{o,ij}$ does not depend on the type of carrier gas used, which means that the elution time can be shortened by use of an adsorptive carrier gas without any detrimental effect on the relative retention, as long as the surface of the separatory column is homogeneous with respect to the adsorption. The experimental results for the D_2–HD system confirmed this prediction within a θ_{NH_3} range between 0.3 and 1.0, as shown in Fig. 10. For the D_2–p-H_2 system, however, the separation factor was unexpectedly dependent on θ_{NH_3} within its whole range. This was found to be due to the catalytic conversion described previously.

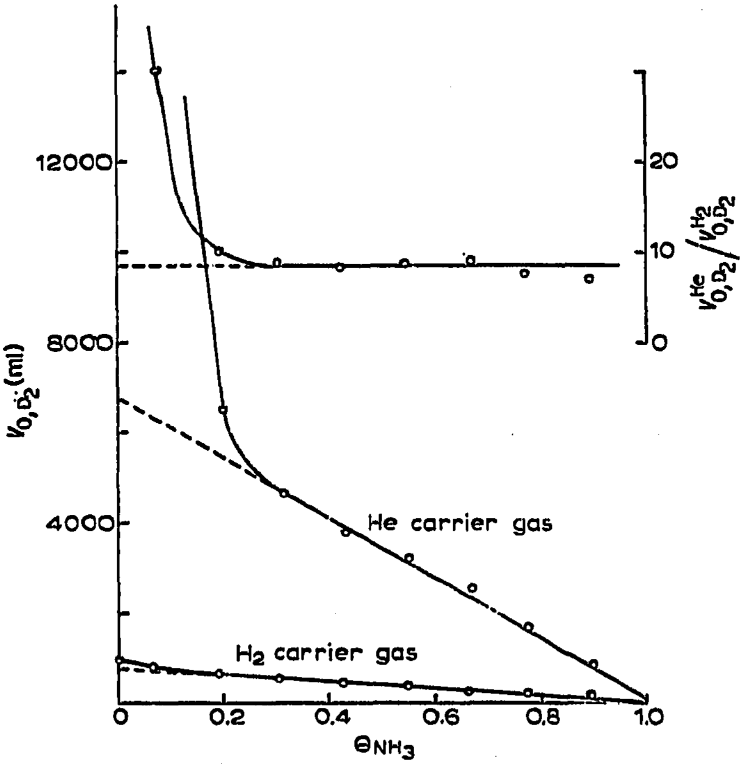

Fig. 9. Relation between θ_{NH_3} and V_{0,D_2} and also between θ_{NH_3} and the ratio of V^{He}_{o,D_2} to $V^{H_2}_{o,D_2}$. Column temperature: −195°C.

TABLE II

THE LANGMUIR CONSTANTS OF HYDROGEN ISOTOPES

Method	θ_{NH_3}	b_{H_2} (*atm*$^{-1}$)		b_{D_2} (*atm*$^{-1}$)	
		−195°C	*−183°C*	*−195°C*	*−183°C*
Adsorption	0.300	7.48	2.87	—	3.31
	0.497	7.14	2.87	11.35	2.61
	Mean	7.31	2.87	11.35	2.96
Gas chromatography	0.3 ~ 1.0	7.32	2.50	—	—

Temperature dependence of retention volume

Differentiating eqn. 9 with respect to $1/T$, we obtain,

$$\mathrm{d}\ln V^{\mathrm{He}}_{0,i}/\mathrm{d}(1/T) = -(Q_i + RT)/R$$

Since $Q_{D_2} \approx 1500$ cal/mole and $RT \approx 180$ cal/mole at —195 °C, we obtain an approximation to the Clausius-Clapeyron equation

$$\mathrm{d}\ln V^{\mathrm{He}}_{0,D_2}/\mathrm{d}(1/T) \fallingdotseq -Q_{D_2}/R \tag{14}$$

Similarly, from eqn. 10, we obtain

$$\mathrm{d}\ln V^{\mathrm{H_2}}_{0,D_2}/\mathrm{d}(1/T) \fallingdotseq -(Q_{D_2} - Q_{H_2})/R \tag{15}$$

by assuming that $Q_{D_2} - Q_{H_2} \gg RT$ and $b_{H_2}p_{H_2} \gg 1$.

Thus it can be safely stated that the temperature dependence of the retention volume with helium carrier gas is essentially bigger than that with hydrogen carrier gas, because Q_{D_2} is always bigger than $Q_{D_2} - Q_{H_2}$. Experimental results showed that when the column was cooled down from —183° to —195 °C, the retention volume, within a θ_{NH_3} range between 0.3 and 1.0, increased 3.7 times for helium carrier gas, but only 1.4 times for hydrogen carrier gas. Approximate isosteric heat of adsorption, estimated by eqns. 14 and 15, was in good agreement with that obtained from the adsorption data, as seen in Table I.

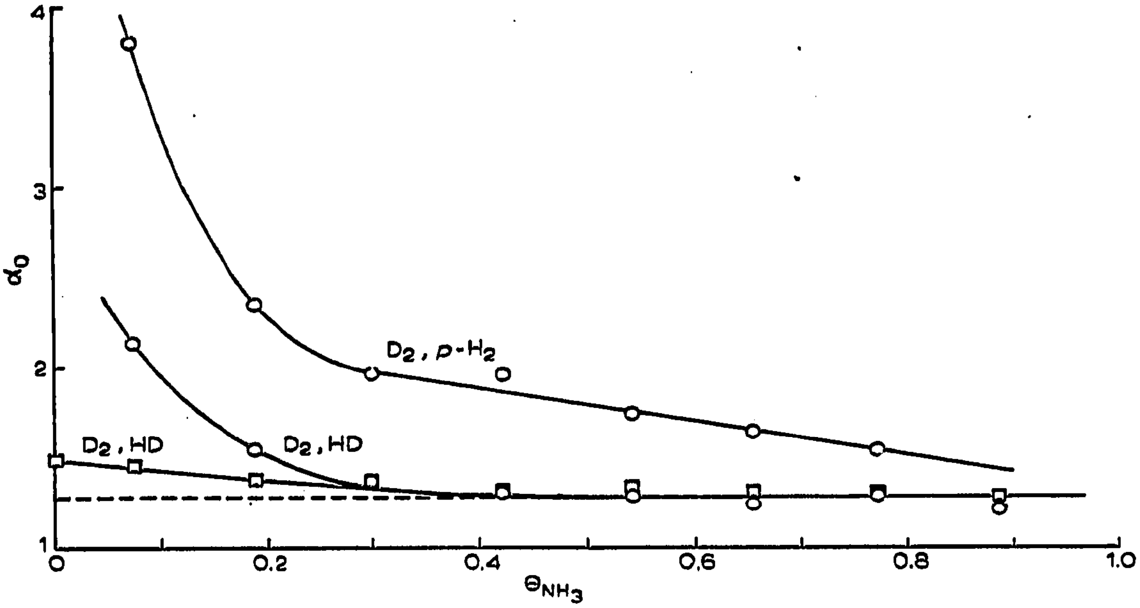

Fig. 10. Relation between α_0 and θ_{NH_3}. ○, helium carrier gas; □, hydrogen carrier gas. Column temperature: —195 °C.

Results in low θ_{NH_3} region

The chromatographic behavior in the region of θ_{NH_3} less than 0.3 is considerably different from that described before, as seen in Figs. 9 and 10: in the case of helium carrier gas, the retention volume depends markedly on θ_{NH_3} and on sample size (*cf.* Figs. 5(d) and 6(b)) and the separation factor at zero sample size is not constant. Furthermore, there is bad tailing of peaks in the chromatogram. These experimental facts cannot be explained by the present theory. That is to say, the surface is strongly heterogeneous with respect to the adsorption. This conclusion is consistent with that from the adsorption experiment. In the case of hydrogen carrier gas, however, the characteristics of the chromatograms do not deviate so much from the theoretical predictions. All these facts suggest that hydrogen carrier gas itself blocks adsorption sites which are too strong and thus unsuitable for the elution chromatography. This is another important effect of hydrogen carrier gas for the present system.

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