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Note

Effect of pH on the gas chromatographic behaviour of silica gel

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Silica gel is one of the popular adsorbents[1–4] used in gas chromatography (GC), and belongs to the second type of specific adsorbent in Kiselev's classification[5]. The effects of chemical and geometrical structure[5,6] of the surface of silica gel and the effects of various thermal[7,8] and chemical [9–11] pre-treatments on its GC behaviour have been studied previously. However, unlike organic porous polymers[12,13], the effects of the conditions of synthesis on the GC behaviour of silica gel have not been elucidated.

Recently in our laboratory the effects of gel pH and the conditions of washing on the surface properties of silica gels and their influence on the moisture adsorption capacity have been studied[14]. In this work we have studied these gels in order to establish the effect of gel pH on their GC behaviour.

EXPERIMENTAL

The experiments were performed on a CIC (Chromatography and Instruments Co, Baroda, India) gas chromatograph equipped with a katharometer detector and Omniscribe (Digital Electronics Ltd., Bombay, India) Series 5000 strip-chart recorder complete with an integrator.

Samples of silica gel were prepared by acidification of sodium silicate solutions. The gel was washed with distilled water until it was free from electrolytes. The detailed method of preparation of these gels has been reported earlier[14,15]. The gel was ground and the fraction of 80–100 mesh was evenly packed in copper columns (2 mm I.D.) by a conventional method. Hydrogen was used as the carrier gas. The columns were activated at 200°C for 2 h under a stream of hydrogen before use. The samples were injected with a 2-ml Chirana gas-tight syringe (Laboratory Instruments, Prague, Czechoslovakia).

The specific retention volume (V_g) was calculated from the expression

$$V_g = j\,[F_C(t_R - t_A)/W_L]\;273/T$$

where F_C is the volume flow-rate measured at the column outlet with a soap-bubble flow meter and corrected to the column temperature (T) and outlet pressure, and t_R, t_A, W_L and j are the retention time of the sorbate, the dead retention time, the weight of the sorbent in the column and the pressure correction factor, respectively. The

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peak asymmetry was expressed as the ratio of the distances of the front and the rear of a peak as measured at one tenth of the peak height, from the perpendicular from the peak maximum to the time coordinate[16].

RESULTS AND DISCUSSION

The effect of gel pH on the chromatographic selectivity of silica gel towards permanent gases is depicted in Fig. 1. The chromatographic selectivities of these gels were compared in terms of their ability to separate a mixture of air, carbon monoxide and methane. A decrease in selectivity of the gel as the pH increases from 1.1 to 4.1 is apparent. The best separation was achieved with silica gel prepared at pH 1.1 and this separation is even slightly better than that achieved earlier[1].

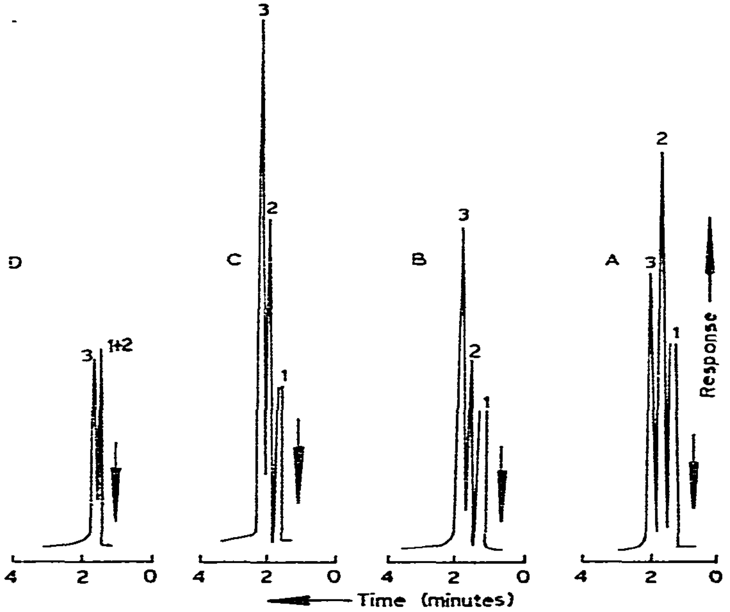

Fig. 1. Effect of gel pH on the GC selectivity of silica gel. Column, 2 m × 2 mm I.D.; temperature, ambient (32–33°C); flow-rate, 30 ml/min. pH: A, 1.1; B, 2.6; C, 4.1; D, 11.0. Peaks 1, air; 2, carbon monoxide; 3, methane.

For practical purposes silica gel of high surface area produced at a low pH is suitable for the separation of common gases and a gel with a low surface area is unsuitable for this separation (Fig. 1D).

A graph of pressure drop (ΔP) *versus* volume flow-rate for columns packed with silica gels produced at different pHs is shown in Fig. 2. The broken line is the average drawn through all the points. Although the lines obtained with individual gel are fairly straight, they vary around the average line within experimental error (*i.e.*, column-to-column reproducibility). Similar results were obtained at ambient temperature. The column permeability is thus independent of the gel pH and is significantly lower than that of Chromosorb P.

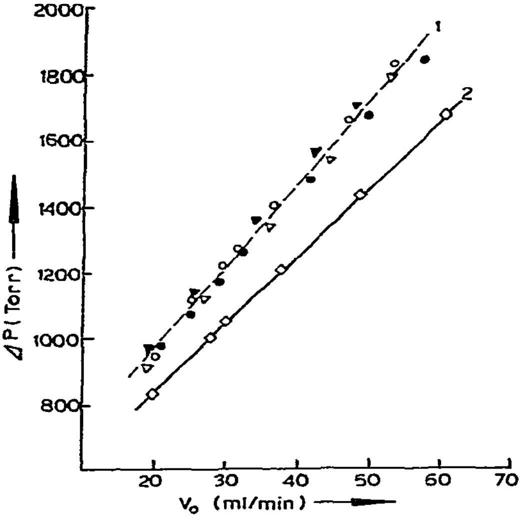

Fig. 2. Plots of pressure drop (ΔP) *versus* volume flow-rate on silica gel. Column, 2 m × 2 mm I.D.; temperature, 100°C. pH: ○, 1.1; ●, 2.6; △, 4.1; ▲, 11.0. □, Chromosorb P.

In Fig. 3, the pressure drop at a flow-rate of 30 ml/min in columns packed with different silica gels and Chromosorb P is plotted against column temperature. The results indicate that the gel pH has no effect on the temperature dependence of the column permeability. The packing structure of the bed seems to be virtually unaffected by the gel pH.

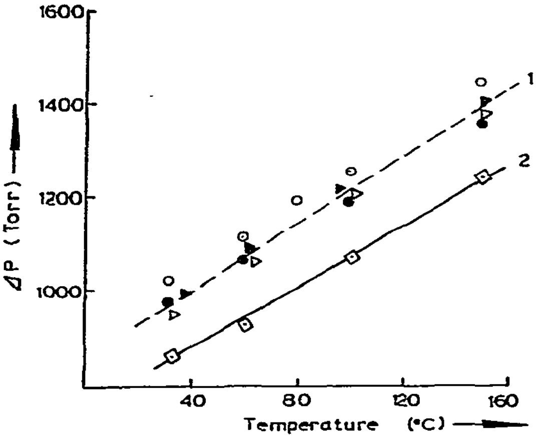

Fig. 3. Plots of ΔP *versus* column temperature on silica gel. Column, 2 m × 2 mm I.D.; flow-rate, 30 ml/min. Symbols as in Fig. 2.

The graphs of log V_g *versus* $1/T$ for these gels are shown in Fig. 4. The parallel lines indicate that the heat of sorption is independent of gel pH. It therefore follows that the chemical nature of the surface is independent of gel pH. With Porasils (porous silica beads), Feltl and Smolková[4] observed an approximately constant concentration

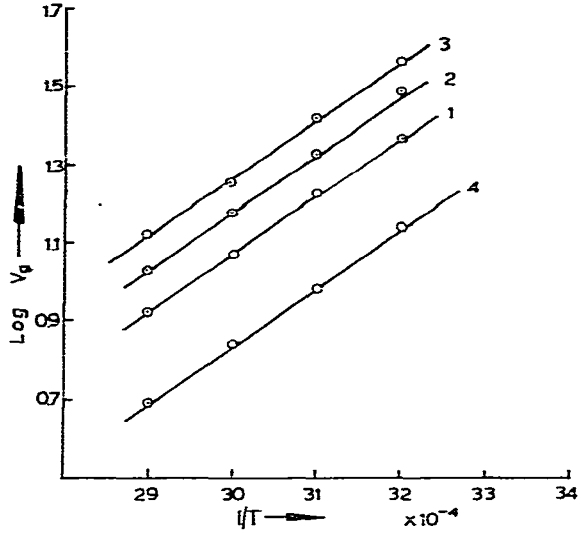

Fig. 4. Plots of log V_g for carbon dioxide *versus* $1/T$ on silica gel. Column, 1.4 m × 2 mm I.D. pH: 1, 1.1; 2, 2.6; 3, 4.1; 4, 11.0.

of hydroxyl groups on the surface and this group is believed generally to be the only specific interaction centre on these surfaces.

Some interesting results of the effect of gel pH on the capacity ratio (k') for carbon dioxide are shown in Table I, together with BET surface area determined from the sorption of nitrogen. Although the surface area decreases with increase in gel pH, k' increases significantly up to pH 4.1 followed by a drastic decrease at pH 11.0.

TABLE I

EFFECT OF GEL pH ON CAPACITY RATIO (k') FOR CARBON DIOXIDE

Column, 1.4 m × 2 mm I.D.; temperature, 70°C; flow-rate, 30 ml/min.

Gel pH	*Capacity ratio (k')*	*Surface area*[14] *(m^2/g)*
1.1	6.8	858
2.6	10.1	759
4.1	10.3	486
11.0	2.6	190

In order to understand quantitatively the interaction between the sorbate and the sorbent surface, the effective surface area available to the sorbate molecule rather than the true surface area determined by the sorption of nitrogen should be considered. As the gel pH increases, the entire pore spectrum shifts to larger pore diameters[17]. As a result, it is expected that the effective surface area available to the carbon dioxide molecule will increase with increasing gel pH up to a certain stage, and thereafter it may decrease. The increase in k' value with increasing gel pH up to pH 4.1 is thus explained. A similar observation with Porasils was made by Feltl and Smolková[4].

Earlier Guillemin *et al.*[3] found that, anomalies occur in the dependence of the sorption of butene-1 on Spherosils on the surface area, and they explained this phenomenon by a change in the concentration of the so-called reactive hydroxyl groups. The active hydroxylgroups or reactive groups are determined by selective silanization with trimethylchlorosilane. Their conclusion cannot be considered to be authoritative as the results for the reactive hydroxyl groups were related to unit weight of the adsorbent. For direct comparison the results should be related to unit surface area. Further, the values of the specific surface areas determined by the sorption of nitrogen should be replaced with the values obtained by the adsorption of a sorbate of similar structure. Feltl and Smolková[4] treated the data of Guillemin *et al.*[3] in this way and did not find any anomaly.

In adsorption chromatography, peak asymmetry can stem from the surface heterogeneity of the sorbent. The effect of gel pH on peak asymmetry is depicted in Table II. The peak asymmetry increases with increase in gel pH. With gels of pH 4.1 and 11.0 very tailed peaks were found even when the needle volume of the gas was injected. Hence the surface heterogeneity seems to increase with increasing gel pH.

TABLE II

EFFECT OF GEL pH ON THE PEAK ASYMMETRY FOR CARBON DIOXIDE

Column, 1.4 m × 2 mm I.D.; temperature, 70°C; flow-rate, 30 ml/min; sample load, 0.2 ml.

Gel pH	*Peak asymmetry*
1.1	0.75
2.6	0.69
4.1	0.47
11.0	0.31

The structural heterogeneity and the heterogeneity of the adsorption force field of silica gels are known to increase with decreasing average pore size[5]. However, the present results are contrary to this general behaviour. An irregular shape of the curve was also observed earlier[3] on plotting the asymmetry as a function of the specific surface area of Spherosils.

The rate of polymerization of silicic acid varies with pH. The growth of particles of polymers in the pH ranges 9.5–9 and below 2 is due mainly to the polymerization between monosilicic and polysilicic acids, and in the pH range 7–4 mainly to the random condensation of all the polymer species with each other[18]. In acidic solutions, the size distribution of the polymers is symmetrical, whereas a broad and random distribution of particle sizes of the polymers arises from a random condensation of all the polymer species with each other (pH 4–7). A random condensation mechanism may result in a very uneven distribution of the various silanol groups on the surface. The structural heterogeneity (especially with respect to pore shape) and the heterogeneity of the adsorption force field of these gels probably stem from this condensation mechanism. Although we could not include a large number of gel samples in our study, the results on peak asymmetry seem to be related to this pH-dependent condensation mechanism.

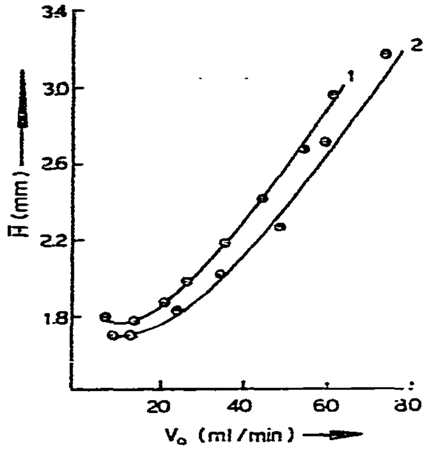

Fig. 5. Effect of carrier gas flow-rate on $\bar{H}$ for carbon dioxide. Column, 1.4 m × 2 mm I.D.; temperature, 70°C. pH: 1, 1.1; 2, 2.6.

The effect of carrier gas flow-rate on the apparent plate height ($\bar{H}$) for the gels produced at pH 1.1 and 2.6 is depicted in Fig. 5. In order to obtain symmetrical peaks the experiments were conducted at a high sensitivity, injecting only the needle volume of gas. Similar plots for the other gels could not be made owing to considerable peak tailing. The slopes of the lines in the mass-transfer predominant flow-rate region are virtually identical. Hence the total non-equilibrium mass transfer coefficients for carbon dioxide are virtually identical for these gels. An increased eddy diffusion contribution to $\bar{H}$ is apparent for the gel produced at pH 1.1 relative to that produced at pH 2.6. However, for practical purposes this difference is not very significant.

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REFERENCES

1 P. G. Jeffery and P. J. Kipping, *Gas Analysis by Gas Chromatography*, Pergamon Press, New York, 1964.
2 R. J. Leibrand, *J. Chromatogr. Sci.*, 5 (1967) 518.
3 C. L. Guillemin, M. LePage and A. J. deVries, *J. Chromatogr. Sci.*, 9 (1971) 470.
4 L. Feltl and E. Smolková, *J. Chromatogr.*, 65 (1972) 249.
5 A. V. Kiselev, *Advan. Chromatogr.*, 4 (1967) 113.
6 A. V. Kiselev, Yu. S. Nikitin, R. S. Petrova, K. D. Schcherbakova and Ya. I. Yashin, *Anal. Chem.*, 36 (1964) 1526.
7 L. Feltl, P. Lutovský, L. Sosnová and E. Smolková, *J. Chromatogr.*, 91 (1974) 321.
8 D. F. Cadogan and D. T. Sawyer, *Anal. Chem.*, 42 (1970) 190.
9 C. S. G. Phillips and C. G. Scott, in J. Purnell (Editor), *Progress in Gas Chromatography*, Interscience, New York, 1968, p. 121.
10 A. F. Isbell, Jr. and D. T. Sawyer, *Anal. Chem.*, 41 (1969) 1381.

11 A. G. Datar and P. S. Ramanathan, *J. Chromatogr.*, 114 (1975) 29.
12 E. N. Fuller, *Anal. Chem.*, 44 (1972) 1747.
13 H. Hradil and J. Lukáš, *J. Chromatogr.*, 172 (1979) 85.
14 T. Saran, I. B. Paul, D. S. Chatterjee, L. V. Ramachandran and P. N. Mukherjee, *J. Appl. Chem. Biotechnol.*, 28 (1978) 633.
15 T. Saran, I. B. Paul, D. S. Chatterjee, L. V. Ramachandran and P. N. Mukherjee, *The Preparation of Desiccant Grade Silica Gel*, C.F.R.I. Report, Central Fuel Research Institute, Bihar, 1979.
16 T. A. Gough and C. F. Simpson, *J. Chromatogr.*, 51 (1970) 129.
17 T. Saran, I. B. Paul, L. V. Ramachandran and P. N. Mukherjee, *J. Appl. Chem. Biotechnol.*, submitted for publication.
18 K. Shimada and T. Tarutani, *J. Chromatogr.*, 168 (1979) 401.