Surface Characterization Including Surface area measurements of the Chromatographic Silica gel

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Summary:Structural system of silica gel has been investigated by adsorption techniques and Electron Microscopy. The gel is highly porous and primarily composed of large irregular grains which are disorderly arranged, constituting the voids. Heat treatment shrinks the material of the gel on the expense of bound water. Most of the surface area and pore volume lie in the small pores with hydraulic radii than 20°A.

Introduction

Silica gel is frequently employed for adsorption of gases and liquids. It is specially used for chromatographic purposes. As the structure of the porous adsorbents play a very important role in the adsorption process [1-2], it was decided to investigate the pore structure of the gel. Most of the work done on the porous nature of the adsorbents [3-7] assume the cylindrical pore structure, hence the surface area, pore volume and pore radii were calculated on the basis of Kelvin equation.

If the structure of the porous adsorbent is highly intermingled network with narrow constrictions of different sizes [8-10] then these parameters could be determined accurately by a method which does not assume any shape of pores. In this paper, therefore, effort has been made to utilize Kiselev's equation [11] for investigating the structure of the gel.

Experimental

Silica gel, whitish in colour, 60-120 mesh size, manufactured by BDH, England, was specified for chromatographic adsorption.

Carbon tetrachloride, n-hexane, methyl alcohol were of analytical grade and were not treated further. Benzene was purified and distilled over phosphoric oxide.

Free water (moisture) was determined by drying the silica gel in an oven at 150°C. Heating, cooling and weighing was continued until constant weight was obtained between successive weighings.

Dehydration of the sample was performed by heating the gel at high temperature for one hour in the muffle furnace. For determination of densities, the samples were heated at 500°C for one hour and were evacuated under the respective fluid, in a vacuum desiccator. Specific gravities were then determined in the standard specific gravity bottles. Bulk densities were determined in containers of known volume while the mercury density was determined in pure and clean mercury using mercury pycnometer.

Total pore volume was determined by finding the geometrical and true volumes [8] of the gel in the mercury and boiling distilled water respectively. Accessible pore volume to the fluids of different molecular size was assessed in the same way.

Specific surface area was determined by a method originally inspired by Kiselev [11]. For this purpose pure water vapours were adsorbed at different relative pressure at 288 K.

Electron microscopy was tried to obtain a direct and unambigous evidence of the textural arrangements of the particles of the gel. The system was examined under S.E. microscope Mini Scan Hitachi Akashi at the Department of Biology, Quaid-i-Azam University. The micrographs were taken by Polaroid Camera at 50 x magnification.

Results and Discussion

Surface area was determined from adsorption isotherm (Fig.1) by applying the following equation derived by Kiselev's [11].

$$S = \frac{1}{\alpha} \, as \, ^{ah} -RTLn \, P/_{Po} \, da$$

FIG.(I)
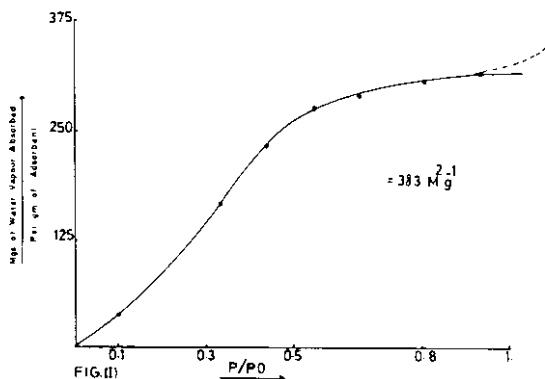
Where S = specific surface area
α = surface tension of the water
as = moles of the water vapours adsorbed at the beginning
ah = moles of the water vapours adsorbed at saturation
R = Gas constant
T = Absolute temperature
P/Po = Relative Pressure
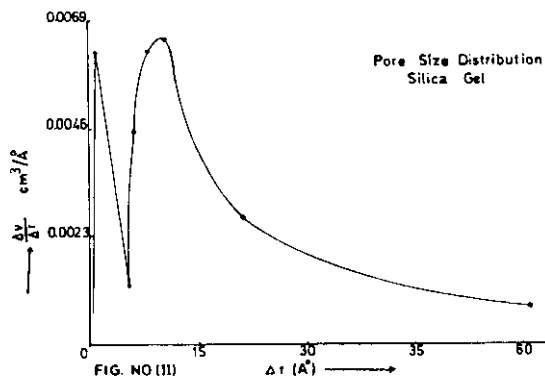da = Total number of moles taken up by the adsorbent.

Surface area was calculated by graphical integration and the result is given in Table 1.

Total pore volume was calculated by the density method [9] which comes out to be $0.62 \, ccg^{-1}$. Micropore volume was obtained from adsorption-isotherm by applying Gurvitsch rule [13,14].

Macropore volume was obtained by subtraction.

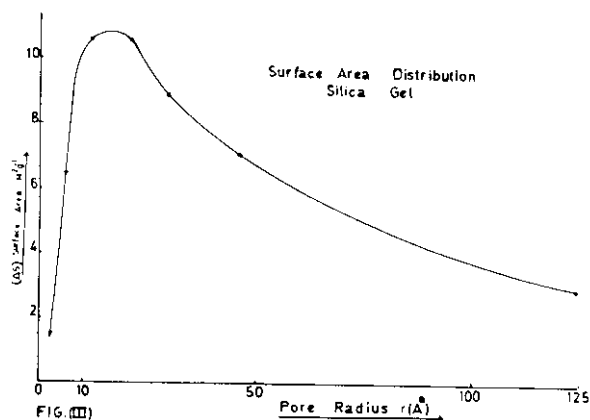Table-1:Experimental values of the physical parameters of the silica gel.

S.No.	Parameter	Value
1.	Free water	3.42%
2.	Boundwater (at 1000°C)	8.21%
3.	True density (Boiling water)	$2.43 \, gcc^{-1}$
4.	Specific surface area	$383 \, m^2 g^{-1}$
5.	Total Pore Volume	$0.62 \, ccg^{-1}$
6.	Micropore volume	$0.32 \, ccg^{-1}$
7.	Transitional/ Macropore volume	$0.30 \, ccg^{-1}$
8.	Average pore radius	$16 \, \overset{\circ}{A}$
9.	Total pore length	$1.88 \times 10^{10} cmg^{-1}$
10.	Bulk density (Loose)	$0.633 \, gcc^{-1}$
11.	Bulk density (Packed)	$0.711 \, gcc^{-1}$
12.	Porosity	60%

FIG. NO (II)

Pore Size Distribution
Silica Gel

that it does not work as a molecular sieve for the sizes of molecules in this range. The results in this table are the averaged over at least three readings. Methyl alcohol unexpectedly gives high value which is due to the fact that the adsorbed layers of CH_3OH on silica surface show high density than the layers away from the silica surface. This problem has been encountered by some research workers, working on the other systems with CH_3OH [14].

Average pore radius was calculated to be 16A. Pore volume and pore distribution were obtained by stepwise analysis of the isotherm (Fig.1). Pore size distribution (Fig. II) shows that most of the pore volume is contained in the pores having radii 10 A or less. This means that gel is mainly composed of small and transitional pore.

Surface area distribution graph (Fig.III) indicates that large portion of the surface area lies in the pores range of 10-15 A radii.

Pore volume accessible to the fluids of different sizes is given in table II. Accessible pore volume is nearly the same for these fluids which means

Electron micrograph (Photostate is not clear) Fig. IV/a which has been pictured manually (Fig. IV/b) shows that the gel is basically composed of large and irregular grains – giving rise to voids.

The effect of heat on the gel structure was examined in terms of bulk densities – which are the masses per unit volume of the container. The results (Fig. V) indicate that the bulk-densities increase with increased heat treatment, showing shrinkage of the individual grains, with corresponding removal of bound water. This is supported by the dehydration curve (Fig. VI).

FIG.(III)
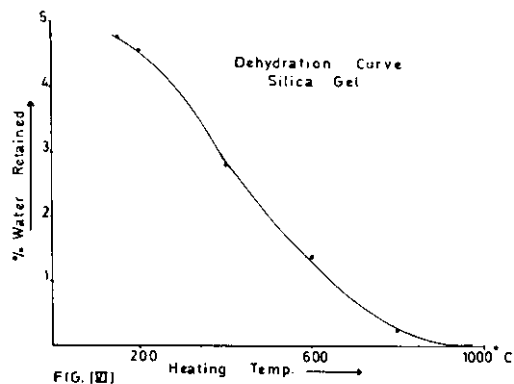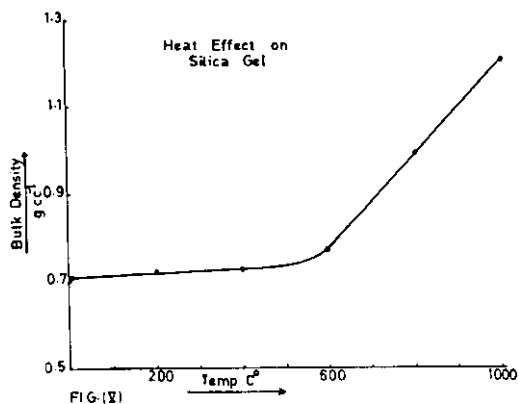
Surface Area Distribution
Silica Gel

Fig : IV

Heat Effect on Silica Gel

FIG-(IV)

Dehydration Curve Silica Gel

FIG. (V)

Table-II: Accessible pore volume, to the Fluids of different molecular sizes.

No.	Fluid	Molecular size	Accessible Poro volume ccg^{-1}
1/a	Boiling distilled water	3.5	0.62
1/b	Cold,dist.H_2O	3.5	0.578
2	CH_3OH	4.6	0.599
3.	C_6H_6	5.9	0.568
4	CCl_4	6.1	0.561
5	n-Hexane	6.7	0.553

The shape of the isotherm is very clear type "V" of BDDT classification [15] and it is in agreement with some of the previous research work [15]. This represents a typical example of porous systems and the low pressure portion of the isotherm suggests co-operative adsorption.

Conclusion

Silica gel is primarily composed of large irregular grains which arrange disorderly to give rise to voids. It is highly porous and the pores are mostly small, giving tremendous sur-face area of about 383 m^2g^{-1}.

Average pore radius being 16A, most of the pore volume and surface area lie in the pores having 10-15 A radii.

Acknowledgement

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