

Heats of Adsorption of Chromatographic Silica Gel

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Summary: The structural system of chromatographic silica gel, as investigated by adsorption techniques and electron microscopy is highly porous having 63% porosity and composed of large irregular grains, arrange in disorderly manner, constituting the voids. Treatment at high temperature shrinks the materials on the expense of bound water. Most of the surface area and pore volume lie in the micropores.

Organic vapours such as acetone, methyl alcohol, methyl ethyl ketones and methyl acetate were adsorbed on the gel between 0-37°C under vacuum. The data were taken on Cahn electrobalance- 1000. Isothermic heats of adsorption at number of temperatures and coverages were determined by applying Clausius Clapeyron equation. It is interpreted in terms of activation energies which suggests two types of adsorption processes.

Introduction

Silica gel is frequently employed for the adsorption of gases and liquids. It is specially suited for chromatographic purposes, i.e. for identification and separation of organic and inorganic substances. The structural system of silica gel is investigated by adsorption techniques and Scanning Electron microscopy [1]. Oxygen adsorption on sputtered Si (100) surface and the disappearance of the surface state as the oxide is formed, is previously investigated by X-ray Photoelectron Spectroscopy (XPS) and Ultraviolet Photoemission Spectroscopy (UPS) [2]. Thermodynamics of adsorption [3-5]. Heats of adsorption [6-7] and surface area measurements [8-9] of various adsorbents is previously investigated. The values of isosteric heats of adsorption were calculated by applying Clausius Clapeyron equation to the adsorption isosters at constant surface coverage and different temperatures as

$$q_{se} = \frac{2.3R \log P_2/P_1}{1/T_1 - 1/T_2} \quad (1)$$

where the symbols have their usual meaning.

Results and Discussion

Water vapour adsorption isotherm is shown in Fig. 1. The shape of the water vapour adsorption is very clear type-IV isotherm of BDDT classification [10]. This represents typical example of porous systems and the low pressure region of the isotherm suggests cooperative adsorption. The surface area

calculated from Kiselve's equation [11] is 383 m²/g is comparable to the results of surface area calculated through BET method, i.e. 359 m²/g. The surface area calculated by nitrogen adsorption isotherm come out as 348 m²/g and this agreement is due to the fact that water interact physically with the surface having crosssectional area of 1.08 nm instead of 1.48 nm. This observation is previously made by other workers [12-15]. Use of scanning electron microscope for the determination of surface area, yield lower values as 146 m²/g. It may be due to the fact that the particle is observed externally, thus leaving out area consisting of capillaries and pores. Secondly it observe the particle only two dimensionally.

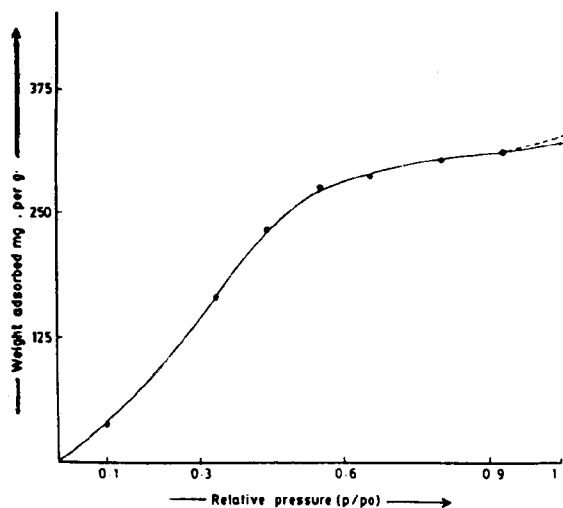


Fig.1: Water vapour adsorption isotherm on silica gel.

Dehydration curve of silica gel is shown in Fig. 2. It is evident from the curve that dehydration occurs in two steps. In the first step loss of 16% wt in temperature range of 40-210°C is observed and it is physically adsorbed water. In the second step loss of 6% weight in the temperature range of 400-700°C is observed which is bound water, i.e. H-bonded to SiOH group [16]. At higher temperature the curve is practically parallel to abscissa. The H-bonded water is harder to remove than physically adsorbed water and would therefore be of great importance in many of the application of the silica. The removal of both types of water is necessary to understand their sorption characteristics.

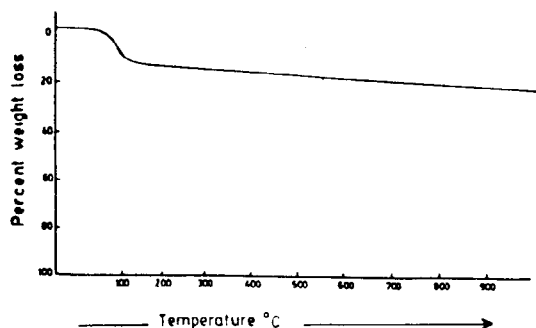


Fig. 2: Dehydration curve of silica gel.

Adsorption isotherm were obtained by plotting weight adsorbed (x/m) in g/g of the gel against equilibrium pressure. Adsorption isosters were calculated from a series of isotherm, by reading pressure and temperature at constant coverage for various organic vapour and gel system. Organic vapours such as acetone, methyl ethyl ketone, methyl acetate and methyl alcohol were adsorbed at different temperatures (0-37°C). The adsorption isotherm were plotted for each system and all the system have the same general shape and follows type-11 isotherm of BDDT classification. As an example adsorption isotherm and isoster of acetone silica system are shown in Fig. 3,4 respectively. Values of isosteric heats of adsorption in kcal per mole from the experimental data at different coverages and temperatures were calculated by applying clausius clapeyron equation and are tabulated in Tables 1-4.

Isosteric heats of adsorption is not the same as the enthalpy change for the adsorption process. The relation between these quantities were given by

Table-1: Acetone/silica

No.	T(°C)	Coverage 0.09 gg ⁻¹ q _{st} Kcal mol ⁻¹	Coverage 0.1101 gg ⁻¹ q _{st} Kcal/mol ⁻¹	Coverage 0.135 gg ⁻¹ q _{st} Kcal mol ⁻¹
1	9	24.768	7.26	22.10
2	18	5.88	13.20	13.47
3	24	19.06	24.35	18.00
4	28	53.63	42.26	24.01
5	33	41.64	24.76	13.51

Table 2 : Methyl alcohol/silica.

No.	T(°C)	Cover 0.12 gg ⁻¹ q _{st} Kcal mol ⁻¹	Coverage 0.1344 gg ⁻¹ q _{st} Kcal mol ⁻¹	Coverage 0.152 gg ⁻¹ q _{st} Kcal mol ⁻¹
1	3	13.587	13.399	13.68
2	9	9.108	8.326	12.39
3	15	11.455	12.032	9.21
4	21	11.970	10.38	11.209
5	27	13.266	9.58	13.24

Table 3: Methyl ethyl ketone/silica.

No.	T(°C)	Coverage 0.1232 gg ⁻¹ q _{st} Kcal mol ⁻¹	Coverage 0.144 gg ⁻¹ q _{st} Kcal mole ⁻¹	Coverage 0.168 gg ⁻¹ q _{st} Kcal mol ⁻¹
1	10	14.70	15.95	13.56
2	16	8.90	10.32	9.31
3	22	8.61	9.24	14.32
4	28	10.10	9.12	16.43
5	34	30.64	30.92	20.65

Table 4: Methyl acetate/silica.

No.	T(°C)	Coverage 0.112 gg ⁻¹ q _{st} kcal mol ⁻¹	Coverage 0.152 gg ⁻¹ q _{st} Kcal mol ⁻¹	Coverage 0.182 gg ⁻¹ q _{st} Kcal mol ⁻¹
1	6	14.40	14.44	15.64
2	12	7.746	9.24	10.08
3	18	15.13	10.15	9.57
4	24	25.292	22.28	17.54
5	30	29.24	19.40	19.67

T.L. Hill [16]. From the data in tables 1-4 it is noted that there are large variation in the observed heats of adsorption, these varying from 3.32 kcal/mole 53.65 Kcal/mole but the most common value lie between 7 and 16 kcal/mole. To amplify the significance of these values complimentary factors like variation with coverage and variation with temperature were calculated. Heats of adsorption as high as 53.63 kcal/mole for adsorption of acetone and 30.92 for the adsorption of methyl ethyl ketone on silica might indicate chemisorption. In general the heats of adsorption obtained are nearly equal to the heats of vapourisation and corresponds to the physical adsorption. Examples for such cases are (14.7, 15.95, and 13.56) kcal/mole for adsorption of methyl ethyl ketone and (14.4, 14.44, 14.64) kcal/mole for the adsorption of methyl acetate.

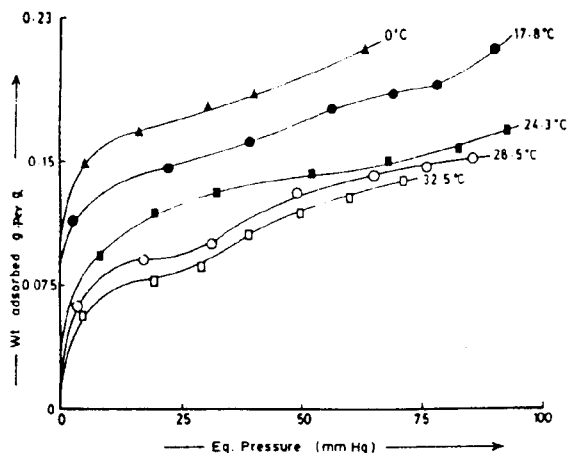


Fig. 3: Adsorption isotherm of acetone on silica gel at various temperatures.

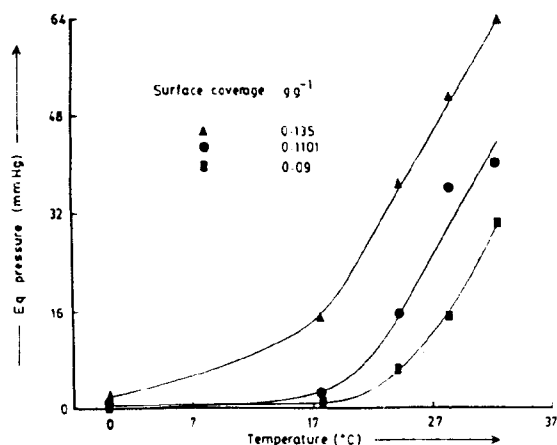


Fig. 4: Adsorption isoster of acetone on silica gel at various temperatures.

A third set of heats of adsorption show values which are less than the heats of vapourisation, L_e of the adsorbate. These exhibits negative net heats of adsorption. It is difficult to interpret the smaller heats of adsorption in terms of physical adsorption or chemisorption because the thermodynamic quantity which determined the adsorption is not the heats of adsorption but the free energy of adsorption. For physical adsorption to occur spontaneously the ΔG and ΔS values may be negative and there may be not change in the chemical bonding of the adsorbate or adsorbent. This implies that ΔH for such system may be negative. However if chemisorption occurs the bonding of the adsorbate and adsorbent may changed and ΔS for such system could be positive or negative. As a result the values of ΔH for such process could be negative and small

or positive and still corresponds to the negative ΔG values for the process. Thus we conclude that small values of heats of adsorption are ambiguous and could corresponds to physical adsorption or to weak chemisorption.

In order to study the behaviour of q_{st} with respect to temperature and as function of coverages. The effect of temperature on the values of q_{st} is explained in terms of activation energy. We assume that two adsorption processes may occurred. The first with low activation energy and the second with high activation energy. Considering the first one, with low temperature process, the adsorption attributable to this will decrease with increase in temperature. When a sufficiently high temperature is reached, the second high activation energy process can begin and the adsorption will decrease with increase in temperature. Considering the heats of adsorption as function of coverage we find for example, that there is sudden rise in some cases, after an initial decrease. Whereas in the case of methanol we find that the heats of adsorption at low and high temperature are constant and roughly independent of coverages. This constancy can be explained in terms of lateral interactions between the adsorbed molecules as the monolayer is approached. Evidence is support of this observation comes from the work of Polley [17] Spencer [18] and other workers [19-20]. They observed both polar and non polar adsorption and find evidence of lateral interactions between the adsorbed molecules.

Experimental

The silica gel selected for investigation was 60-120 mesh size supplied by BDH England. All the adsorptive used were of analytical reagent grade having 99.55-99.9% purity. They were further purified by freezing and thawing method. Benzene was purified and distilled over phosphoric oxide. For the determination of densities the samples were evacuated in container of known volume desiccator. Bulk densities were determined in container of known volume, whereas the mercury density were determined with pure and clean mercury using mercury pycnometer.

Dehydration of the gel was recorded by using Shimadzu thermogravimetric Technique (TGA-31), with temperature programmed furnace fitted with voltage stabilizer, thermocouple and R-122T re-

order. The heating rate employed was 10° C per minute and nitrogen as purge gas at flow rate of 40 ml/min. Adsorption of water vapor on silica gel was performed using saturated solutions of various electrolytes. Saturated solutions of zinc chloride, calcium chloride, potassium carbonate, magnesium nitrate, ammonium nitrate, ammonium sulfate and potassium nitrate with P/P° values 0.1, 0.33, 0.44, 0.55, 0.45, 0.81 and 0.93 respectively. Each solution was then placed in a desiccator covered with tight lid and maintained at room temperature. A known amount 2-3 g of silica powdered was then put in each desiccator and lid were firmly closed. Every four days the change in weight were noted. Equilibrium was attained in six weeks.

Adsorption data were recorded on Cahn-1000 electrobalance in connection with vacuum line, thermoionic, pirani and Mcleod gauge. The gel samples were preheated to 500° C and about 0.1-0.5 g were of the samples, placed in a silica crucible and were placed in weighing unit. Prior to pumping the hang down tube was maintained at a fixed temperature using a constant temperature water circulating thermostated bath. The entire system was subjected to evacuation for at least 30 minutes before taking the data. The pumping was continued until pressure of 10^{-4} to 10^{-5} mbar was achieved. Then the vapour of the desired adsorptive were allowed to be adsorbed until constant weight was attained. The pressure was measured from mercury manometer and the amount adsorbed was recorded on x-y Beckman chart recorder. This process was repeated for higher pressure, in order to obtain an equilibrium pressure in which there is no further adsorption.

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