

Sorption Kinetics of Water Vapours in Chromatographic Silica Gel

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Summary: Adsorbents possess two fundamental properties. One property is the maximum adsorption capacity, which is determined from equilibrium adsorption isotherm. The other property is the adsorption rate constant, derivable from adsorption kinetics. Experimental data on the physical adsorption of water vapour by chromatographic silica gel, at different relative vapour pressures, were used to calculate values for the kinetic adsorption capacity and adsorption rate constant at room temperature. Various types of diffusivities were determined through equations derived by Fick. Total pore volume (0.581 cc g⁻¹) and specific surface area (744 m² g⁻¹) were found by Gurvitsch rule and Kiesel's equation respectively. An average pore radius (hydraulic) is 7.8 x 10⁻⁸ cm as obtained by a new method suggesting shapeless pore model. The study of these quantities provides a strong basis for evaluating surface properties of adsorbent.

Introduction

Silica gel is frequently used for the adsorption of gases and liquids. It is especially suitable for chromatographic purposes *i.e.* for separation of organic from inorganic substances. The physical structure [1-6] of the adsorbent plays an important role in adsorption process. Diffusion of vapours and gases in porous media involves sorption kinetics, thermo-osmotic isobaric and non-isobaric flows, isothermal transient and steady flows etc. The texture of the adsorbents *e.g.* a network combined with narrow constrictions of different sizes, affects the flow of various adsorbates. The kinetics of adsorption of gases/vapours on homogenous microporous materials containing micropore with equal energy are often described by models based on activated surface diffusion. It is assumed that the adsorbent contains macropores and micropores and that there is clear discontinuity in properties between them. Penetration of the gas/ vapour into the micropore implies adsorption and involves a change of phase and the rate of process is determined by the unidimensional activated diffusion of the adsorbate along the length of the pore. In the macropore the adsorbable vapour is assumed to be entirely in the gaseous state, hence adsorption is negligible and diffusion is rapid as compared to surface diffusion that takes place in the micropores. A micropore opens into a macropore and is in contact with a constant supply of gas/ vapour at constant pressure.

The flow sequence involved in the heterogeneous adsorption of a gas/ vapour by a solid adsorbent occurs in the following four sequential steps. 1. Mass transfer (External diffusion), wherein the gas/ vapour molecules are transported from a vicinity of a neighbouring air molecules to a vicinity of the adsorbent granule outer surface. 2. Surface diffusion, wherein gas/ vapour molecules are transported over a two-dimensional granule surface, through to the mouth or entrance of the adsorbent micropore. 3. Intragranular diffusion, wherein the transport of the gas/ vapour molecules within the small pores causes the molecules to collide with or enter into the force field of an active site. 4. Physical adsorption, wherein the adsorbate molecules lose translational freedom and are held by and occupy the active site. The study of these phenomena along with equilibrium sorption has provided firm bases for estimating surface characteristics [7-12]. In this paper an effort has been made to investigate the surface properties and structure of chromatographic silica gel by sorption kinetics and isothermal flow of water vapours.

Results and Discussion

The amount of water vapours adsorbed, was calculated and plotted versus p/p_0 to give adsorption isotherm as shown in Fig. 1.

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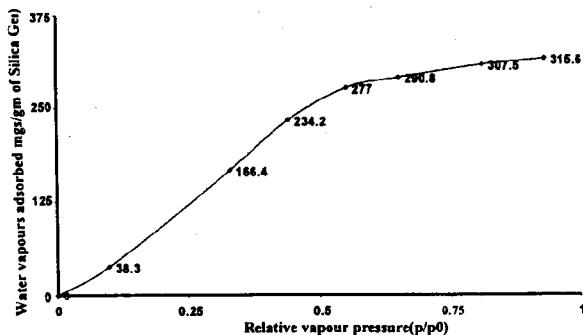


Fig.1: water vapour/Silica System

Various physical constants and parameters of the adsorbate and adsorbent which affect the flow of vapours and gases through the porous media in one way or the other, under prevailing experimental conditions, are given in Table-1. The given data of adsorbent (silica gel) were obtained as before but on a little different sample [14].

Various parameters for the sorption kinetics e.g. rate constant, effective (Overall) diffusivities, Knudsen (micropore) diffusivities etc. were calculated through Fick Type equation [7], as given below. Bulk (macropore) diffusivities were obtained by subtraction.

$$M_t/M_\infty = Q_t - Q_0 / Q_\infty - Q_0 = 1 - 8/\pi^2 \sum_{n=1}^{\infty} 1/(2n+1)^2 \exp[-D(2n+1)^2 \pi^2 t / (2\ell)^2] \quad (1)$$

Which reduces as below:

$$M_t/M_\infty = 2(Dt/\ell^2 \pi)^{1/2} \quad (2)$$

To give:

$$M_t = Q_t \quad \text{and} \quad M_\infty = Q_\infty$$

Where Q_t , Q_0 and Q_∞ are the amounts sorbed at times t , zero and infinity (when equilibrium has been established). These

expressions serve in standard ways to evaluate the rate constant D/ℓ^2 and hence D , the overall diffusivity within the medium.

For intracrystalline diffusion, the equations (1) and (2) are replaced by (3) and (4) respectively as given below. ℓ is the length of the pore which is equal to the pore radius, r_0 , for spherical media. D_i is the Knudsen diffusivity which is found by the simple rearrangement as follows:

$$M_t/M_\infty = 1 - 6/\pi^2 \sum_{n=1}^{\infty} 1/n^2 \exp(-D_i n^2 \pi^2 t / (r_0)^2) \quad (3)$$

$$M_t/M_\infty = 6/r_0 (D_i t/\pi)^{1/2} \quad (4)$$

Results obtained by the above methods are given in Table-2.

$$RC = \text{Rate constant} = D/\ell^2$$

$$ED = \text{Effective diffusivities} = D = \text{Overall diffusivity}$$

$$KD = \text{Knudsen diffusivities} = D_i = \text{micropore diffusivity}$$

$$BD = \text{Bulk diffusivities} = (ED - KD) = \text{macropore diffusivity}$$

Water vapours adsorption on silica gel gives type V₁ isotherm (Fig.1) of BDDT classification. This indicates porous nature of the solid with internal surface area [13]. These isotherms are characterized by their being convex to pressure axis, suggesting that the adsorption is co-operative in nature; the more molecules are adsorbed, the easier it is for further molecules to get adsorbed. The attraction of adsorbate molecules for each other now exceeds to their attraction for the adsorbent. The shape of the isotherm shows that the adsorption capacity of the gel for water vapours increases less steeply at the beginning which means that all the vapour molecules reaching the surface of the adsorbent enter slowly with gradual

Table-1: Physical Constants/Parameters of Adsorbate/ Adsorbent

S. No	Adsorbate (water)	S. No	Adsorbent (silica gel)
1.	Molecular Size 3.5 Å	1.	Specific Surface Area 744 m ² g ⁻¹
2.	Molecular Volume 18 cc g ⁻¹	2.	Total Pore Volume 0.581 cc g ⁻¹
3.	Dielectric Const. 80.36 (20 °C)	3.	Average Pore Radius (hydraulic) 7.8 x 10 ⁻⁸ cm
4.	Vapour Pressure 0.023 atm (20 °C)	4.	Total Pore length 1.5 x 10 ¹³ cm g ⁻¹

Table-2: Water Vapours/ Silica System

S.No.	P/P ₀	Time hours	RC. cm hr ⁻¹	ED. cm ² hr ⁻¹	KD cm ² hr ⁻¹	BD cm ² hr ⁻¹
1.	0.1		X10 ⁻³	x10 ⁻¹⁷	x10 ⁻¹⁸	x10 ⁻¹⁷
		168	12.76	7.77	8.63	0.86
		264	5.13	3.12	3.46	2.77
		360	2.93	1.78	1.98	1.58
		456	1.91	1.16	1.28	1.03
2.	0.33	168	5.21	3.17	3.52	2.82
		264	2.95	1.79	1.99	1.59
		360	2.21	1.34	1.46	1.19
		456	1.71	1.04	1.16	0.93
		576	1.44	0.87	0.97	0.77
3.	0.44	168	3.63	2.21	2.46	1.96
		264	2.70	1.64	1.83	1.46
		360	2.06	1.25	1.39	1.11
		456	1.65	1.01	1.12	0.89
		576	1.36	0.83	0.92	0.74
4.	0.55	168	3.58	2.17	2.42	1.93
		360	2.09	1.27	1.42	1.13
		456	1.67	1.02	1.13	0.91
		576	1.36	0.83	0.92	0.74
		648	1.21	0.74	0.82	0.66
5.	0.65	168	4.00	2.44	2.70	2.16
		264	3.00	1.84	2.05	1.64
		360	2.24	1.36	1.52	1.21
		456	1.77	1.08	1.20	0.96
		576	1.42	0.86	0.96	0.77
6.	0.81	648	1.21	0.74	0.82	0.65
		168	3.60	2.21	2.46	1.96
		264	2.94	1.79	1.99	1.59
		360	2.16	1.32	1.46	1.17
		456	1.71	1.04	1.15	0.93
		576	1.36	0.83	0.92	0.73
		648	1.20	0.73	0.82	0.65
7.	0.93	792	0.99	0.60	0.67	0.54
		888	0.88	0.54	0.59	0.48
		168	4.50	2.71	3.02	2.41
		264	2.92	1.77	1.97	1.57
		360	2.15	1.31	1.45	1.16
		456	1.70	1.04	1.15	0.92
		576	1.35	0.82	0.91	0.73
		648	1.20	0.73	0.81	0.65
		792	0.98	0.60	0.66	0.53
		888	0.88	0.53	0.59	0.47
		960	0.81	0.49	0.55	0.44

adsorption. Therefore, the rate controlling step is both internal diffusion and physical adsorption. The adsorption capacity of the gel becomes invariant between 0.6 and 0.7p/ p₀. The flat portion of the isotherm indicates completion of the monolayer. Here, the rate controlling step is the physical adsorption. In the last portion (> 0.75 p/ p₀), the isotherm tends to rise very slightly and reaches the saturation line at a finite angle. This shows multilayer adsorption and capillary/ bulk condensation, representing filling of all the pores with adsorbate in ordinary liquid form. Pore size distribution of the silica gels [14] shows that most

of the pore volume is contained in very small pores having radii 10 Å or less which means that the silica gels are mainly composed of small and transitional pores.

Table-2 shows a gradual and small decrease in the parameters such as rate constant, effective (overall) diffusivities, Knudsen (micropore) diffusivities and bulk (macropore) diffusivities. All these results indicate that the surface (both internal and external) is gradually being covered and the active sites are being occupied, hence the rate of adsorption decreases. The decrease in all diffusivities further represents the filling and blockage of the pores with the passage of time.

This effort has been made to demonstrate and explain the sorption rate and flow of water vapours in the silica gel system. In general, the diffusion of vapours in porous structure is very complicated to obtain appropriate measurements and their interpretation.

Experimental

Chromatographic silica gel, 60-120 mesh size manufactured by BDH, England, was selected for the investigation. Properly saturated (with single solute) solutions of zinc chloride, magnesium chloride, potassium carbonate, magnesium nitrate, ammonium nitrate, ammonium sulphate and potassium nitrate were prepared in fresh distilled water from the analytical grade reagents in carefully greased vessels, with a suitable capacity to provide different constant relative pressure ranging from 0.1 to 0.93 p/p₀ respectively [13]. The gel samples were heated to 500 °C for one hour and cooled to room temperature before weighing. Then, suitable amounts (5-10 gms) of a sample were placed in each of the container of a porcelain crucible. Time and date were noted and each of the samples was weighed again after some time (say four days) until a constant weight was obtained.

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