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Diffusion and Flow of Water Vapours in Chromatographic Alumina Gel

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Abstract

The kinetics of sorption of water vapours in chromatographic alumina gel was studied. Water vapours are adsorbed on the gel at temperature (15 °C) at different constant relative pressure from 0.1-0.93 p/p. Rate constant, Effective diffusivities, Knudsen diffusivities and bulk diffusivities were determined through Fick type equation. Total pore volume is 0.498 cc g^{-1} and specific surface area comes to be 465 m^2 g^{-1} as obtained by Gurvitsch rule and Kieselve's equations respectively. An average pore radius (hydraulic) is $1.1x10^{-7}$ cm. The study of these quantities provide a strong basis for evaluating surface properties.

Introduction

Alumina gel is frequently used for the adsorption of gases and liquids. It is specially suitable for chromatographic purposes i-e for separation of organic and inorganic substances. The physical structure of the adsorbent plays an important role in adsorption process [1-6]. 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 study of these phenomenon along with sorption equilibrium gives firm bases for estimating surface characteristics [7-12]. In this paper an effort has been made to investigate the surface properties of chromatographic alumina gel by sorption kinetics and isothermal flows of water vapors.

Experimental

Chromatographic alumina gel, 60-120 mesh size, manufactured by BDH, England, was selected for the investigation. Properly saturated (when no more solute was dissolved) 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 constant relative pressures from 0.1 to 0.93 p/p_0 respectively [13]. The gel samples were heated to 500°C for one hour and cooled to room temperature before weighing. Then suitable amount (5-10 gms) of treated sample was placed in porcelain crucible in each of the containers (vessels).

Time and date was noted and each of the sample was re- weighed after certain time interval (say four days) until constant weight was obtained.

The amount of water vapours adsorbed, was calculated and plotted versus p/p_0 to give adsorption isotherm as shown in Figure 1 [14].

Results and Discussion

Various physical constants and parameters of the adsorbate and adsorbent which effect 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 (alumina gel) in Table 1 was obtained as before on a little different sample by the authors previously [15].

Various parameters for the sorption kinetics e-g rate constant (D/ℓ), effective diffusivities (D), Knudsen diffusivities (D_i) were calculated through Fick type equation [8] as given below. Bulk diffusivities (D_a) were obtained by subtraction.

$$M_t/M\infty = Qt - Q_0/Q_\infty - Q_0 = 1 - 8/\pi^2 \sum_{n=0}^{\infty} 1/(2n+1)^2 \exp - D(2n+1)^2 \pi^2 t/(2\ell)^2 \quad (1)$$

Which reduces as below

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

Now

$M_t = Q_t$ and $M_\infty = Q_\infty$

Where

Q_t, Q_0 and Q_∞ are the amounts sorbed at times t, zero and infinity (when equi-librium 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. Rearrangement is given as below. ℓ is the radius of the medium.

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

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

$$[\,(M_t/M\infty/2)\,]^2 = [(\,Dt/\ell^2\,\pi\,)^{1/2}\,]^2$$

$$[\,(M_t/M\infty\ /2)\,]^2 = Dt/\ell^2\,\text{л}$$

$D/\ell^2 = [(M_t/M\infty/2)]^2 \times \text{л}/t$ -------------- (This is the rate constant).

Now

$D = D/\ell^2 \times \ell^2$ ---------------- (This is the Overall diffusivity).

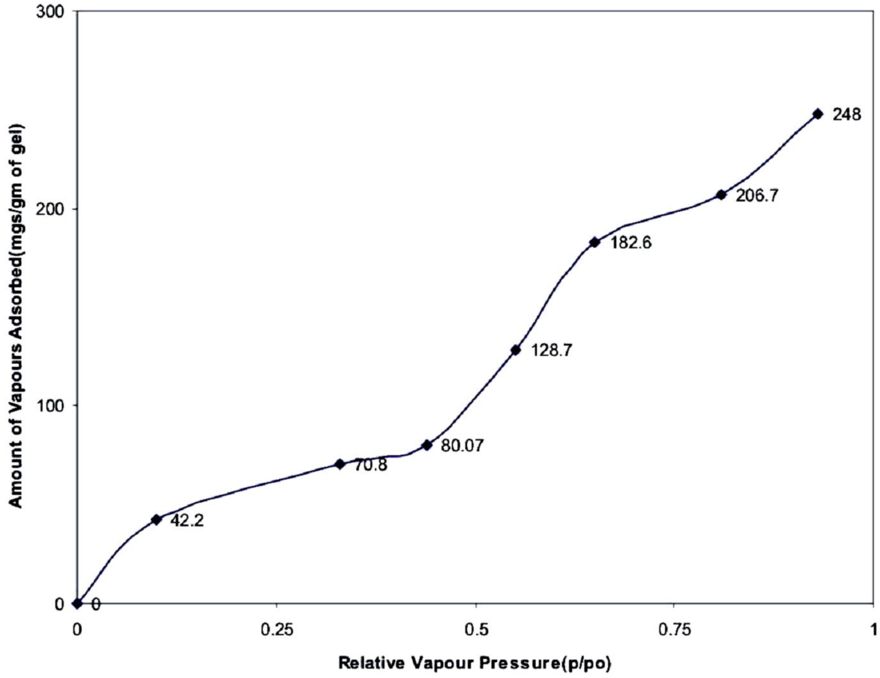

Fig. 1 Water Vapours / Alumina gel System

For intracrystalline diffusion the equations (1) and (2) are replaced by (3) and (4) respectively as given below. ℓ is equal to the pore radius, r_0 for spherical media. D_i is the Knudsen diffusivity which is found as below [8].

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

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

Equation No. (4) is rearranged as below

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

$$[\, M_t/M_\infty \text{ x } r_0/6 \,] = (D_i \, t/\pi\,)^{1/2}$$

$$[\, M_t/M_\infty \text{ x } r_0/6 \,]^2 = [\, (D_i \, t/\pi\,)^{1/2} \,]^2$$

$$D_i \, t/\pi = [M_t/M_\infty \text{ x } r_0/6]^2$$

$D_i = [M_t/M_\infty$ x $r_0/6]^2$ x π/t--------------(This is the Knudsen diffusivity).

Results calculated by the above methods are given in Table 2.

RC = Rate constant = D/ℓ^2

ED = Effective diffusivities = D = Overall diffusivity

KD = Knudsen diffusivities = D_i = micropore diffusivity

BD = Bulk diffusivities = D_a = (ED-KD) = macropre diffusivity

Table 1. Physical Constants/Parameters of Adsorbate / Adsorbent

S. No.	Adsorbate (water)		S. No	Adsorbent (alumina gel)	
1.	Molecular Size	3.5(Å)	1.	S. Surface Area	465 $m^2 g^{-1}$
2.	Molecular Volume	18 cc g^{-1}	2.	Total. Pore Vol.	0.498 cc g^{-1}
3.	Dielectric Const.	80.36 (20 °C)	3.	Avrage Pore Radius.	1.1×10^{-7} cm
4.	Vapour Pressure.	0.023 atm (20 ° C)	4.	Total. Pore length	6.9×10^{12} cm g^{-1}

Table 2. Water Vapours / Alumina System

S. No.	P/P_0	Time hours	RC.cm hr^{-1}	ED.cm^2 hr^{-1}	KDcm^2 hr^{-1}	BDcm^2 hr^{-1}
1.	0.1		$x10^{-3}$	$x10^{-17}$	$x10^{-18}$	$X10^{-17}$
		168	2.80	3.38	3.77	3.00
		264	2.50	3.07	3.42	2.73
		360	2.09	2.54	2.82	2.26
		624	1.22	1.42	1.64	1.25
		720	1.09	1.32	1.46	1.17
2.	0.33	168	11.57	13.99	6.66	13.32
		264	11.22	13.57	4.11	13.16
		360	02.17	02.62	2.92	02.33
		624	01.26	01.52	1.69	01.35
		720	01.09	01.32	1.46	01.17
3.	0.44	168	3.10	3.75	4.14	3.33
		264	2.66	3.22	3.58	2.86
		360	2.00	2.42	2.77	2.14
		624	1.20	1.45	1.67	1.28
		720	1.10	1.33	1.46	1.18
4.	0.55	168	2.95	3.58	3.98	3.18
		264	2.22	2.69	2.99	2.39
		360	1.74	2.11	2.34	1.87
		624	1.15	1.39	1.55	1.23
		720	1.01	1.22	1.36	1.08
5.	0.65	72	3.79	4.59	5.10	8.75
		264	2.10	2.55	2.83	4.85
		360	1.83	2.21	2.45	4.21
		720	1.03	1.25	1.39	2.38
		960	0.80	0.97	1.07	1.84
6.	0.81	72	3.95	4.78	5.29	4.26
		168	2.87	3.48	3.85	3.10
		264	2.54	3.08	3.40	2.74
		360	2.13	2.58	2.85	2.29
		624	1.25	1.52	1.67	1.35
		720	1.09	1.32	1.46	1.18
7.	0.93	72	4.89	5.93	6.59	5.27
		264	2.50	3.03	3.36	2.69
		360	2.01	2.43	2.70	2.16
		720	1.01	1.22	1.35	1.08
		960	0.76	0.92	1.02	0.82
		1320	0.58	0.71	0.79	0.63
		1440	0.54	0.66	0.73	0.59

Adsorption capacity of the alumina gel with water at 288 K is given in Figure 1. This indicates that capacity of the gel for water vapours increases less steeply at the start which means that all the molecules reaching the surface of the gel, enter very slowly with gradual adsorption. Therefore, the rate controlling step is both internal diffusion and physical adsorption. At the beginning the isotherm is a convex to the pressure axis, which indicates the porous nature of the gel with internal surface area. The adsorption capacity becomes almost invariant between 0.3-0.4 p/p_0. This flat portion of the isotherm shows competion of the monolayer. Here the rate controlling step is the physical adsorption. Beyond $0.5p/p_0$, isotherm tends to rise upward, showing multilayer adsorption. In the last portion, having a slight horizontal movement (0.65-0.75 p/p_0), the isotherm rises very slowly reaching the saturation line. This shows capillary/bulk condensation in the pores.

Tables 2 shows 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 covered and the active sites are being occupied, hence the rate of adsorption decreases. The decrease in all diffusivities 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 an appropriate measurements and their interpretation. It is a large area for further research.

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