

# Diffusion of Ethyl Methyl Ketone, Methyl Alcohol and Acetyldehyde Vapours in Chromatographic Alumina Gel

<sup>1</sup>M. KHAN AND <sup>2</sup>M. AFZAL

<sup>1</sup>Department of Chemistry, University of Peshawar, Peshawar, Pakistan  
<sup>2</sup>Department of Chemistry, Quaid-e-Azam University, Islamabad, Pakistan

(Received 9th June, 1994, revised 18th November, 1995)

**Summary:** Organic vapours such as ethyl methyl ketone, methyl-alcohol and acetaldehyde were adsorbed on the alumina gel between 273 K-298K under vacuum of  $10^{-4}$  to  $10^{-5}$  mm Hg, achieved by rotary and oil diffusion pumps. Cahn 1000 electro-microbalance and X-Y Beckman chart recorder were used for recording the data. Kinetic parameters such as rate constant, Knudsen diffusivities, bulk diffusivities and effective diffusivities were evaluated through Fick type equation. The effect of temperature on the sorption of these organic vapours has also been discussed.

## Introduction

Transport phenomenon in porous structures consists of sorption kinetics, thermo-osmotic, isobaric and non isobaric flow, isothermal transient and steady flows etc. The study of these processes along with the sorption equilibrium provides strong foundation for determining the surface properties. Alumina gels are widely used for adsorption and catalytic processes of gases and liquids, and chromatographic purposes [1-6, 10-14]. The structure of an adsorbent plays an important role in adsorption processes (M. Afzal, M. Khan, *J. Chem. Soc.* 9, (3) (1987). The structural system and heats of adsorption has already been investigated (M. Afzal, M. Khan *et al.*, *colloid polym. Sci.*, 269, 483-489, 1991) [7-9]. The present paper deals with the sorption of organic vapours such as ethyl methyl-ketone, methyl alcohol and acetaldehyde alumina systems and various kinetic parameters for these isothermal flow systems are reported.

## Results and Discussion

Various physical constants of the adsorbates which affect the flow of the vapours and gases through the porous media in one way or the other, under prevailing experimental conditions are given in the Table-1,2. Average pore radius of the gel is  $1 \times 10^{-7}$  cm as calculated by Gurvitsch rule.

The plots of amount sorbed vs time for these organic vapours-alumina systems at different temperatures are shown in Figures 1 to 3. These systems follow exothermic behaviour and amount sorbed decreases with increase in temperature i.e.

Table-1: Physical constants of the adsorbates

No.	Adsorbate Name	Mol.Size Å	Mol.Vol. cc g <sup>-1</sup>	Dipole moment μ(D)
1.	E.M.K.	6.01	90	2.78(g)
2.	Methyl alcohol	4.60	40-42	1.71
3.	Acetaldehyde	5.14	56	2.27

Table-2: Vapour pressure of the pure adsorbates

No.	Adsorbate Name	Temperature K	Pressure mm Hg
1.	E.M.K.	273	30
		297	100
2.	Methyl alcohol	273	35
		293	95
3.	Acetyldehyde	273	320
		297	870

the total sorption is less at higher temperature than at low temperature for each system. This is because the energy acquired at higher temperature favours the desorption as both adsorption and desorption phenomena continue simultaneously. Various parameters for sorption kinetics e.g. rate constant, over all (Effective) diffusivities, micropore (Knudsen) diffusivities and macropore (Bulk) diffusivities were calculated by applying the equation as given below [15-19]:

$$Mt/M_{\infty} = Q_t - Q_0/Q_{\infty} - \theta_0 = 1 - 8/\pi^2 \sum_{n=1}^{\infty} 1/(2n+1)^2 \exp - \frac{D(2n+1)^2 \pi^2 t}{(2l)^2} \quad (1)$$

which for large times reduce to

$$Mt/M_{\infty} = 1 - 8/\pi^2 \exp - D\pi^2 t/(2l)^2 \quad (2)$$

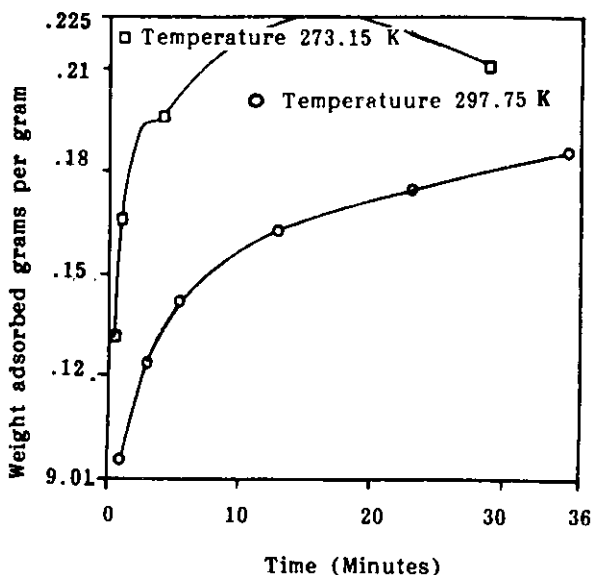


Fig. 1: Adsorption vs Time, E.M.K/Alumina system.

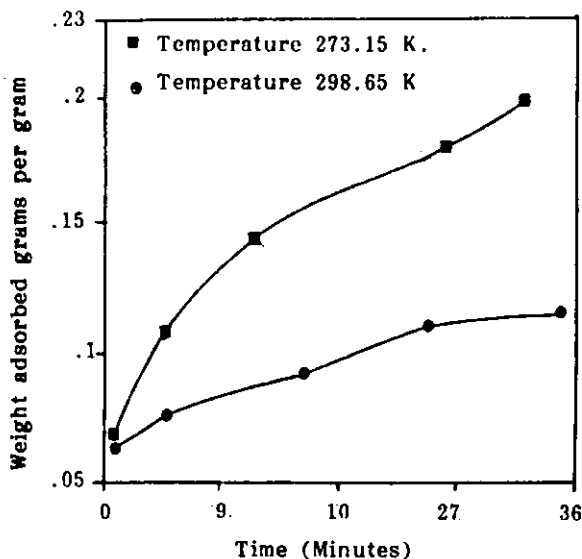


Fig. 2: Adsorption vs Time, Methyl alcohol/Alumina.

and for small time reduce to

$$M_t/M_\infty = 2 (Dt/l^2\pi)^{1/2} \text{-----(3)}$$

where

$Q_t$ ,  $Q_0$  and  $Q_\infty$  are the amounts sorbed at times  $t$  to zero and infinity (when equilibrium has

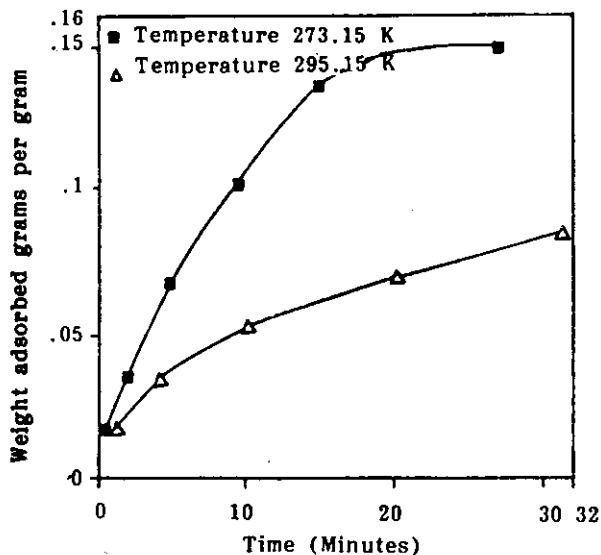


Fig. 3: Adsorption vs Time, Acetaldehyde/Alumina.

been established).  $D/l^2$  is the rate constant and  $D$  is the overall diffusivity within the medium,  $l$  is the length of the pore which is equal to the pore radius  $r_0$  for spherical media.

For intracrystalline diffusion, the equations 1,2 and 3 are replaced respectively by 4,5 and 6 as below.

$$M_t/M_\infty = 1 - 6/\pi^2 \sum_{n=1}^{\infty} 1/n^2 \exp - (Dn^2\pi^2t)/(r_0)^2 \text{-----(4)}$$

$$M_t/M_\infty = 1 - 6/\pi^2 \exp - (D\pi^2 t)/(r_0)^2 \text{-----(5)}$$

$$M_t/M_\infty = 6/r_0 (Dt/\pi)^{1/2} \text{-----(6)}$$

Those systems which reached to equilibrium in nearly 20 minutes, have been evaluated by short time equations and those systems which reached to equilibrium in more than 20 minutes are subjected to long time equations.

Results calculated by the above methods are given in Tables 3 to 5.

$$RC = \text{rate constant} = D/l^2$$

ED = Effective (overall) diffusivity

KD = Knudsen (micropore) diffusivity

BD = Bulk (macro-pore) diffusivity.

Adsorption curves of different adsorbates at alumina gel, adsorbent are plotted vs time at different temperatures and are given in Figures 1 to 3. These curves show that the amount sorbed increases nearly steeply at the beginning especially at low temperature for all the systems which means that all the gas molecules reaching the surface of the adsorbent are immediately moved into the internal pores of the gel and adsorbed by the active sites. The rate controlling step is external diffusion, as the gas molecules cannot reach the outer surface of the adsorbent rapidly enough. After certain initial period (2-10 minutes depending on the system) the adsorption capacity becomes almost invariant. Here the rate controlling step is both internal diffusion and physical adsorption.

The Tables-3 and 4 show gradual and small decrease in the parameters such as rate constant, micro, macro and overall diffusivities. However this gradual decrease in parameters is very small in comparison with overall increase in adsorption as shown by the sorption curves of these systems (Fig. 1, 2).

The gradual fall in rate constant shows that the active sites per unit volume are becoming occupied with the passage of time. The decrease in various diffusivities support the argument in terms of flow hindrance due to completion of monolayer and capillary condensation and some pore blockage. A small increase in the parameters near equilibrium as shown by some systems seems to be the result of capillary condensation.

Acetaldehyde/alumina system behaves in some different way. All the parameters increase slowly over the observed range of time (Table-5). Adsorption capacity becomes nearly invariant as usual after certain initial time (Fig. 3). This may be due to the fact that the vapour pressure of acetaldehyde is many times higher in comparison with other gases and vapours (Table-2). This is in good agreement with our previous research work (acetaldehyde/silica system). In the initial stages the adsorption capacity of acetaldehyde/alumina and also of methyl alcohol/alumina at high temperatures increase but little which show that though adsorbate molecules are freely available and they easily move to the outer surface of the adsorbent cannot rapidly enter inside the structure

Table-3: Ethyl methyl ketone/alumina, system.

Temp. K	Time S	RC $s^{-1}$ $10^{-3}$	ED $cm^2 s^{-1}$ $10^{-17}$	KD $cm^2 s^{-1}$ $10^{-18}$	BD $cm^2 s^{-1}$ $10^{-17}$
273	120	6.35	7.27	15.4	5.73
	240	4.22	4.84	10.7	3.77
	600	2.18	2.49	5.69	1.92
	840	1.71	1.96	4.50	1.51
	1200	1.41	1.62	3.76	1.24
	1560	1.31	1.49	3.53	1.14
298	120	2.44	2.79	4.22	2.37
	240	1.85	2.21	3.91	1.82
	600	1.12	1.28	2.37	1.04
	840	0.94	1.07	2.29	0.841
	1200	0.81	0.929	2.05	0.724
	1920	1.10	1.26	2.98	0.962

Table-4: Methyl alcohol/alumina system

Temp. K	Time S	RC $s^{-1}$ $10^{-4}$	ED $cm^2 s^{-1}$ $10^{-18}$	KD $cm^2 s^{-1}$ $10^{-18}$	BD $cm^2 s^{-1}$ $10^{-18}$
273	240	9.42	10.78	1.31	9.47
	480	7.33	8.39	1.40	6.99
	720	6.45	7.38	1.38	6.00
	1200	5.38	6.67	1.39	5.28
	1440	6.10	6.98	1.51	5.47
	1800	8.0	9.16	2.10	7.06
	291	240	13.9	15.9	2.56
480		9.2	10.5	1.94	8.56
720		7.8	8.93	1.77	7.16
1200		6.89	7.88	1.69	6.19
1800		7.71	8.89	2.02	6.87

Table-5: Acetaldehyde/alumina system

Temp. K	Time S	RC $s^{-1}$ $10^{-4}$	ED $cm^2 s^{-1}$ $10^{-18}$	KD $cm^2 s^{-1}$ $10^{-18}$	BD $cm^2 s^{-1}$ $10^{-18}$
273	240	5.13	5.88	0.079	5.80
	480	6.89	7.89	1.28	6.61
	840	9.43	10.78	2.30	8.48
	1200	11.90	13.60	3.14	10.50
	1440	13.50	15.40	3.62	11.80
295	240	4.87	5.58	0.006	5.57
	600	5.42	6.21	0.996	5.21
	840	5.23	5.99	1.10	4.89
	1200	5.11	5.85	1.18	4.66
	1440	5.39	6.18	1.31	4.86
	1680	6.29	7.21	1.60	5.60

or cannot easily adsorb on the sites, hence the rate controlling step is both internal diffusion and physical adsorption. Its low molecular size and greater dipole moment favour its continuous increase in rate constant and slow increase in diffusivities over the observed range of time.

In this paper an effort has been made to explain and demonstrate the sorption rates and diffusion in porous structures with special reference to alumina gel. The subject is very much complicated and hard enough to obtain suitable measurements and their interpretation. Infact it is a vast field for further investigation.

### Experimental

The alumina gel selected for investigation is whitish in colour, designated as aluminum oxide Fluka basic type 5016 A, for chromatography. All the samples of alumina gel were heated at 773K for one hour and cooled in a vacuum desiccator. All the adsorptive used were of analytical reagent grade, having 99.5-99.9% purity. They were further purified by freezing and thawing method. Adsorption data were recorded on cahn 1000 electro balance in connection with vacuum line, followed by rotary and oil diffusion pumps, Mcleod and Pirani gauges and Beckman X-Y chart recorder. The sample (0.1-0.5 g) was placed in silica crucible and the hangdown tube was maintained at a fixed temperature using constant temperature water circulating thermostatic bath. The entire system was subjected to evacuation for at least 30 minutes before taking data. The pumping was continued until the vacuum of  $10^{-4}$   $10^{-5}$  torr was achieved. Then the vapours of the desired adsorbate were introduced until constant weight was attained. The pressure was measured by mercury monometer with the help of cathometer and the amount sorbed was recorded on X-Y Beckman chart recorder at different interval of time [6-9].

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