ADSORPTIVE DRYING OF ISOPROPYL ALCOHOL ON 4A MOLECULAR SIEVE: EQUILIBRIUM AND KINETIC STUDIES

by

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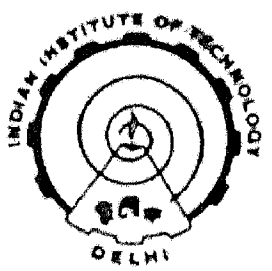
Thesis submitted
in fulfilment of the requirements
for the award of the degree of

DOCTOR OF PHILOSOPHY



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NEW DELHI-110016

MAY, 1995

CERTIFICATE

This is to certify that the thesis entitled **Adsorptive Drying of Isopropyl Alcohol on 4A Molecular Sieve: Equilibrium and Kinetic Studies** presented by Anil K. Jain, is worthy of consideration for the award of the degree of the **Doctor of Philosophy** and is a record of the original bonafide research work carried out by him under my guidance and supervision and that the results contained in it have not been submitted in part or in full to any other University or Institute for award of any Degree.

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ACKNOWLEDGEMENT

It is my pleasure to acknowledge Sh. O.P. Amar for his supervision with keen interest in the research work and cooperation during the course of investigation and timely help even in the odd hours.

It is with a deep sense of gratitude and indebtness that I would like to thank my teacher Prof. A.K. Gupta, Department of Chemical Engineering, I.I.T. Delhi for guiding throughout my research program. I am overawed by his commitment to research and research students. I shall remember him forever for inculcating within me the qualities of confidence, perseverance and a sense of commitment towards one work. It was from him I have learnt how to execute ideas into reality I also thank him for teaching basics of chemical engineering particularly mathematics of diffusion so beautifully, even coming from chemistry background, I could incorporate it into thesis work.

I would like to place on record my sincere thanks to Prof. K. Vasudeva, Department of Chemical Engineering, for taking personal interest in the research work and suggesting the problem and scope for the present work. His valuable suggestions and stimulating discussions are sincerely acknowledged.

I am profoundly thankful to Prof. D. Suba Rao, Head, Department of Chemical Engineering for his concern about my work and clarifying certain doubts about diffusion and adsorption in packed columns and porosity measurements. Encouragement and constant support given by Dr. V.K. Srivastava, Dr. S.K. Gupta, Dr. S.C. Dhingra throughout my thesis work is greatly acknowledged.

At this moment, I would like to recall Dr. T.S.R. Prasada Rao (now, Director, IIP, Dehradun), Dr. S.G.T. Bhat and Dr. R.V. Jasra of IPCL, Vadodra for evoking my interest so immensely in the adsorption studies on zeolites for the first time. during my M.Tech project that I was tempted to continue work on zeolites during the Ph.D. program also.

I would like to acknowledge the assistance received from R.D. Tiwari, Satish, R.K. Pandey and Rirkoo Ram in completing the experimental work. I wish to thank Dr. S.S. Sambi for providing help in the vapour phase studies on TGA instrument and Dr. A. Gupta of TERI, Delhi for porosity measurements.

The efforts of Saji C.G. who skilfully typed the difficult and often illegible manuscript and Sewa Ram who traced many of the figures are sincerely appreciated.

I wish to thank my colleagues and friends, Dr. Manoja, Dr. Navaneeta, Dr. Sushmita, Dr. Shoba, Geetanjali, Ajay, Satyender, Pai, Vipan, Harinder, Mukul, Rahul for maintaining a 'live' atmosphere and making my stay at IIT a unique experience, which I would relish for the rest of my life.

I am indebted to my parents for their constant support and encouragement.

Finally I am greatful to the CSIR, India for awarding me Research Associateship during the course of this work.

[ANIL K. JAIN]

ABSTRACT

INTRODUCTION

In the process industries it is often necessary to dry fluids before these can be used further. The effect of moisture in fluids can lead to decreased catalyst activity or poisoning of catalyst, lower reaction yield, accelerated corrosion or plugging of lines by ice or hydrate formation. Adsorptive drying is an energy efficient process for drying at very low water concentration levels.

The proper design, optimization of adsorption seperation and drying process requires detailed knolwedge of both the equilibria and kinetics of adsorption systems. Solids with bidispersed pore system like zeolite molecular sieves find applications in a wide variety of adsorption systems. The rate at which these processes take place depend on the rate of transport by diffusion in the pore network of the adsorbent.

In porous media, transport of adsorbate is a complex phenomena. Development and design of adsorption process requires complete knowledge of transport mechanism in such solids. As a result, most models for diffusion in porous solids are approximate. A type of biporous model which assumes that porous particle of interest is comprised of numerous microporous particle, is widely studied. Examples include the work of Ruckenstein et al. (1), Haynes and Sharma (2), Wakao and Smith (3), Smith (4,5) and Ruthven (6).

The present work lays emphasis on the study of kinetics of adsorption, and to obtain diffusion parameters for biporous cylindrical particle (molecular sieve zeolite) using rigrous analysis (biporous model) as well as simpler models.

AIM AND SCOPE

The system chosen in the present study is water - isopropyl alcohol - 4A molecular sieve. Experimental equilibrium and kinetic data have been collected.

The kinetic data were interpreted with the help of different models for adsorption. Rigorous analysis for adsorption in biporous solid for cylindrical pellet was applied and values of diffusion parameters for microspheres and macropores were obtained. Simpler models, mainly, homogenous-sphere model and homogenous-cylindrical model were also used to correlate the experimental data and corresponding diffusion values were obtained. Attempt has been made to employ kinetic parameters obtained from the rigrous analysis to correlate the kinetics of adsorption of water vapour from air.

EXPERIMENTAL

Molecular sieve used were of type 4A, 1.6 mm cylindrical pellets (IPCL Catad Division, India). Molecular sieve pellets were activated at 300°C under vacuum for 6 hours before using for any experimental study (7).

The equilibrium studies were carried out in a specially designed glass cell with a high vacuum stopcock and silicon rubber septum for solvent mixture introduction. Aqueous solution of isopropyl alcohol was prepared from known amount of distilled water and analytical grade isorpopyl alcohol. Known amount of molecular sieve (2-5 g) was activated in the cell and liquid mixture of known composition (5-6 g) was injected into the cell through septum and allowed to equilibrate in a constant

temperature bath for 24 hours with occasional shaking. The supernatant solution was analyzed for its water concentration by Karl-Fischer Titrator.

The amount of water adsorbed by molecular sieve was calculated by mass balance. Equilibrium data were obtained in the temperature range 20°C to 70°C over a range of concentrations in fluid phase from 0.02 to 9.2 wt. % of water. It was observed that 1 g of dry molecular sieve could pick up 0.25 g of water and this corresponds to 0.29 g/cm^3 of the cylindrical pellet.

Batch kinetic studies were conducted to study the uptake of water by molecular sieve pellets. A known weight of molecular sieve pellets was activated and transferred to an adsorption vessel (round bottom flask) and immediately stoppered. A known amount of dry isopropyl alcohol (10-11 g, water content $<$ 0.01 wt. %) was already present in the adsorption vessel. A contact time of about 90 minutes was allowed for isopropyl alcohol to diffuse through the macropores of the adsorbent. A known amount of a liquid mixture of isopropyl alcohol and water was introduced into the flask at time zero. The flask was stoppered immediately and kept tightly clamped on a platform type shaker. The motion of the shaker was sufficiently high to minimize the external mass transfer resistance. About 15 samples were drawn periodically during the experiment by syringe and analyzed for their water content. This was continued for about 90 minutes. The final sample was taken 24 hours after the start of the experiment to determine the final equilibrium composition. The initial concentration of water or/and amount of molecular sieve was varied in other runs.

The solution composition was determined as a function of time and water uptake was calculated by material balance. Fractional saturation of molecular sieves was calculated by mass balance and the corresponding equilibrium value.

It is observed that water uptake is rapid initially and decreases later. Also the rate of sorption increases with increase in concentration.

Development of Mathematical Model

An idealized macroporous cylindrical pellet has been considered. It comprises of small uniform spherical microporous crystals (or microspheres). Macropores are assumed to exist in between microspheres. Transport within both macropores and microspheres is assumed to occur by Fickian diffusion. The corresponding coefficients D_p and D_c are assumed to be independent of sorbate concentration. For mathematical simplicity diffusion through both ends of the cylindrical particle is neglected (8).

Macropores are initially filled with non-adsorbing solvent. There is a step change in composition at time zero. The adsorbent particles are assumed to be surrounded by a well mixed solution of finite volume of non-adsorbing solvent and adsorbing component. The adsorbate (water) diffuses in the adsorbent pellet through macropores.

The kinetics of adsorption may be described by the following equation in dimensionless form as:

$$\frac{1}{\alpha}\left[\frac{\partial^2\theta_p}{\partial\eta^2}\right] + \frac{1}{\alpha\eta}\left[\frac{\partial\theta_p}{\partial\eta}\right] = \frac{\partial\theta_p}{\partial\tau} + \frac{\beta}{3\alpha}\left[\frac{\partial\bar{\theta}_c}{\partial\tau}\right]$$

I.C. $\theta_p(\eta,0) = 0$, $\theta_c(\gamma,0) = 0$ for all η

B.C. $\theta_p(1,\tau) = [1-\lambda U(\tau)]$, $\frac{\partial \theta_p}{\partial \eta}(0,\tau) = 0$

where $\lambda = \frac{m\, q_s}{V_l\, C_0}$

$$\eta = \frac{R}{R_p}, \quad \gamma = \frac{r}{r_c}, \quad \theta_p = \frac{C}{C_0}, \quad \theta_c = \frac{q}{q_0}, \quad \tau = \frac{tD_c}{r_c^2}$$

$$\alpha = \frac{D_c/r_c^2}{D_p/R_p^2}, \quad \beta = \frac{3(1-\epsilon)q_0\,\alpha}{\epsilon C_0}$$

$$\frac{\partial}{\partial \gamma}\left[\gamma^2 \frac{\partial \theta_c}{\partial \gamma}\right] = \frac{\partial \theta_c}{\partial \tau}$$

B.C. $\theta_c(1,\eta,\tau) = 1$ for $\theta_p > 0$ $\qquad \frac{\partial \theta_c}{\partial \gamma}(0,\tau) = 0$ for all η

The fractional saturation for a microsphere is given by

$$\bar{\theta}_c = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-n^2\pi^2\tau)$$

$$U(\tau) = 2\int_0^1 \bar{\theta}_c(\eta,\tau)\,\eta\, d\eta$$

Numerical Results

Effect of different parameters: It is expected that the rate of sorption would increase with increase in values of any one or more of the parameters like $C_0(1-\epsilon)q_0$, D_p/R_p^2, D_c/r_c^2. The numerical values of parameters C_0, D_p/R_p^2 were varied in order to see this effect on rate of sorption and extent of penetration of solute in macropores. It was found that by increasing the solution concentration (while keeping the values of other parameters fixed), the pore solution penetrates deeper inside the particle resulting in higher value of fractional saturation U(t) of the pellet. It implies that more and more microspheres are exposed to the adsorbate, as the value of C_0 increases. Similar behaviour was observed when the value of D_p was increased.

Increase in the numerical value of D_c would also result in increase in the rate of sorption. It was found out that with increase in value of D_c, the penetration of the pellet by adsorbate decreases, although the fractional saturation value U(t) increases. It is because of the competitive nature of the two diffusion mechanisms. It may be noted that diffusion in macropores and microspheres takes place simultaneously.

The effect of dimensionless parameters α and β was also looked at.

Correlation of Experimental Data

Correlation of computed results with experimental data has been carried out. Following parameters need to be defined before performing computations; C_0, ϵ, D_p and R_p, q_0, D_c and r_c. Values of $C_0(1-\epsilon)q_0$, R_p are known independently; value of ϵ, (macroporosity of 4A molecular sieve pellet) was determined experimentally by Mercury porosimetry technique and it was found to be 0.236. Pellet diameter R_p was

also measured experimentally and the average value was found to be 1.6 mm. Whereas q_0 is not known independently, sorption capacity of the pellet $(1-\epsilon)\ q_0$ is experimentally determinable.

The macropore diffusion coefficient was estimated as (9)

$$\epsilon\ D_p = \epsilon\ D_m/X$$

The value for tortuosity, X indicated in the literature lies in the range 1.7 to 4.5 for zeolite molecular sieve materials (10-12). In the present computations it was assumed to be 3.

For generating a theoretical uptake curve, all the parameters were known except D_c/r_c^2 which was determined by matching computed results with experimental data. A value of $D_c/r_c^2 = 0.8 \times 10^{-4}$ cm^2/s was found to be suitable for rigrous analysis. It is also possible that another pair of value of D_c/r_c^2 and tortuosity can generate a theoretical uptake curve which correlates experimental data. However the above reported values of parameters D_c/r_c^2 and tortuosity could be successfully used in correlating all the experimental runs for different values of C_0 and λ. However uniqueness of values of D_c/r_c^2 and X cannot be ascertained independently.

Simplified Models

Simplified models are amenable to hand computations whereas rigorous analysis requires computer time, sometime upto more than 2 CPU hours on ICL 3980 mainframe computer, when radius of particle is divided into 50 divisions. Analysis of batch kinetic data were also carried out by simpler models like homogenous spherical model, homogenous cylindrical model.

Homogenous Spherical Model

It was assumed that resistance to mass transfer in macropores is negligible. The adsorbate penetrates through the macropores very quickly and hence all the microspheres of the pellet are exposed to the adsorbate simultaneously.

The following equation for diffusion in a homogenous sphere should correlate the experimental data

$$U(t) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[- n^2 \pi^2 \frac{D_{sp}}{r_c^2} . t \right]$$

Effective diffusion coefficient D_{sp}/r_c^2 was determined from the dimensionless time and real time for the same fractional saturation value. It was found that effective diffusion coefficient D_{sp} varies linearly with initial fluid concentration.

Homogenous Cylindrical Model

The experimental data could also be correlated assuming the pellet to be a homogenous cylinder, since the shape of pellet is cylindrical.

Neglecting the diffusion from the flat ends, fractional saturation for homogenous cylinder is given by the equation (13).

$$U(t) = 1 - \sum_{n=1}^{\infty} \frac{4}{R_p^2 \alpha_n^2} \exp\left[- D_{cy} \alpha_n^2 . t \right]$$

where α_n's are the roots of

$$J_0 (R_p \alpha_n) = 0$$

where $J_0(x)$ is the Bessel function of the first time of order zero.

Computed uptake curve could be matched successfully with experimental data and hence effective diffusion coefficient was determined. The values of D_s varied linearly with initial concentration in the fluid phase. Although this model could be successfully used to correlate the experimental data but it may not give true physical picture (14).

Adsorption of water vapor from air

In the case of adsorption from vapor phase where adsorbate concentration is very low, the external fluid film resistence dominates. It was also felt that tortuosity of molecular sieve pellet and diffusion parameter D_s/r_c^2 should be same irrespective of whether the adsorption is taking place from liquid phase or vapor phase. To confirm this, experiments were conducted for adsorption of water vapor from air on 4A molecular sieve pellet.

Uptake of water was measured in microbalance of thermogravimetric (TGA) instrument. A single pellet of molecular sieve was kept in a stainless steel basket, which was suspended in a cylinderical glass tube with the micro-balance. Air was passed through the tube at a constant flow rate. Change in weight of pellet was measured with time gravimetrically. Concentration of water vapour in air was determined with the help of dry bulb and wet bulb thermometers.

Fractional saturation was found to be varying almost linearly with time particularly during the initial period of adsorption. Vapor phase uptake results were analysed with the help of mass transfer coefficient model to calculate external mass transfer resistance. Numerical results were generated for diffusion in biporous cylindrical pellets incorporating film thickness. Computed results matched with

experimental fractional saturation values by choosing the value of D_c/r_c^2 for microspheres as 0.8 x 10^{-4} cm^2/s and turtuosity as 3, which were also used for correlating liquid phase adsorption data.

To sum up equilibrium and kinetic data for adsorption of water from ispropyl alcohol solution on 4A molecular sieve were obtained and analyzed mathematically with help of biporous model for cylindrical pellet.

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