Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Jain, Anil K. and Gupta, Ashok K.(1994) 'Adsorptive Drying of Isopropyl Alcohol on 4A Molecular Sieves: Equilibrium and Kinetic Studies', Separation Science and Technology, 29: 11, 1461 — 1472
To link to this Article: DOI: 10.1080/01496399408003031
URL: http://dx.doi.org/10.1080/01496399408003031

SEPARATION SCIENCE AND TECHNOLOGY, 29(11), pp. 1461–1472, 1994

Adsorptive Drying of Isopropyl Alcohol on 4A Molecular Sieves: Equilibrium and Kinetic Studies

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ABSTRACT

Batch equilibrium and kinetic studies were carried out for adsorption of water from aqueous solution of isopropyl alcohol on 4A molecular sieves (cylindrical pellets of 1.8 mm diameter). Equilibrium data obtained were rectangular in shape. The adsorption capacity was about 0.25 g water per gram dry adsorbent. This corresponds to 0.29 g water/cm^3 of molecular sieve pellets. The effect of temperature on equilibrium behavior was not significant in the temperature range 20 to 70°C. Batch kinetic studies were carried out at room temperature. Differential equations for the uptake of water by biporous cylindrical particles were written and solved numerically by the finite forward difference method. The macropore diffusion coefficient was estimated by assuming the macroporosity of the pellet to be 0.35 and the value of tortuosity to be 3. The diffusion coefficient for micropores was obtained by matching the computed uptake curve with the experimental data. Assuming the average radius of microspheres to be 1 μm, the diffusion coefficient for micropores was found to be 0.4×10^{-12} cm^2/s.

INTRODUCTION

In the process industries it is often necessary to dry fluids before they 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 a very energy-efficient process, particularly for drying at very

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low water concentration levels. Extensive information is available in the literature indicating the use of a molecular sieve for adsorptive drying.

In early work, Derr and Willmore (1) studied drying of ethyl and butyl acetates, pyridine, and gasoline with activated alumina in a percolation column. Gregor and coworkers (2) were the first to carry out a thorough and systematic study of water removal. They mostly studied drying of air with different ion-exchange resins. Eaves and Sewell (3) studied the finite batch drying kinetics by aluminas, silica gels, molecular sieves, and other chemical drying agents. In later work reporting on adsorptive drying, Teo and Ruthven (4) studied drying of ethanol with 3A molecular sieves and also reported mathematical analysis. Joshi and Fair (5, 6) worked extensively on the drying of nonpolar organic solvents. A mathematical analysis for packed bed was also presented.

The large-scale commercial development of molecular sieves as selective adsorbents for adsorptive drying has stimulated extensive research into the kinetics of sorption in such materials. A commercial molecular sieve pellet consists of thousands of microporous zeolite crystals bound together with the help of a clay binder (7). Thus there are two types of pores in a pellet: macropores between individual zeolite crystals and micropores in zeolite crystals (8).

The rate of mass transfer in such biporous adsorbents is controlled by diffusion in macropores of the pellet as well as in microspheres, in addition to external fluid film resistance. Conditions were controlled in earlier studies in such a way that only one of these was significant, and modeling of experimental data proved to be simpler. Examples of macropore control in batch adsorption experiments include studies of hydrocarbon sorption in Davison 5A pellets by Youngquist et al. (8) and by Ruthven and Derrah (9). Examples of micropore control include the studies of Kondis and Dranoff (10) (ethane in Linde 4A) and those of Ruthven and Loughlin (11, 12) (ethane and *n*-butane in Linde 5A crystals and 100 mesh crushed pellets). Loughlin et al. (13) also studied the effects of crystal size distribution and shape for Linde 4A and 5A zeolites on micropore diffusion and predicted the theoretical uptake curve.

The problem of diffusion in a bidisperse medium was first considered by Sargent and Whitford (14) who obtained a numerical solution to the diffusion problem subject to a change in sorbate concentration at the external surface. A more elegant analytical solution was obtained by Ruckenstein et al. (15), and the solution was used by Ma and Ho (16) to interpret kinetic data for the sorption of allene and methyl acetylene in Linde 13X sieve pellets. Ma and Lee (17) also considered the corresponding problem for a finite volume adsorption system in which the boundary condition at the pellet surface was time-dependent.

All these analyses depend on the assumption of a linear equilibrium relationship. However, for many systems of practical importance, the equilibrium isotherms are highly nonlinear or rectangular. Garg and Ruthven (18) investigated the effects of nonlinearities in the adsorption–desorption isotherm on the pressure swing process. Doong and Yang (19) simplified the equations of material balance by assuming parabolic concentration profiles within the micropores. Recently Peterson (20) modeled adsorption in a bidisperse pore system using the Turner pore structure and developed an analytical solution for micropore uptake.

In the present research group, Anand (21) confirmed that the adsorption behavior of a bidisperse system depends on the relative rates of penetration in the micropores and the macropores. If the micropores are slowly penetrated compared to the macropores, adsorbate will penetrate to the center of the macropores before appreciable penetration in the micropores has taken place. In such a situation the concentration of adsorbent outside the microspheres is almost the same everywhere in the pellet, and adsorption rates are nearly uniform throughout the pellet. Conversely, if diffusion in the micropores is much faster than in the macropores, an adsorbate front progresses toward the center.

AIM AND SCOPE

We are studying the feasibility of drying an organic solvent by commercially available molecular sieve zeolites. Isopropyl alcohol has been chosen as a model organic solvent and 4A molecular sieve as the adsorbent. In preliminary exploratory experiments it was found that the moisture content in isopropyl alcohol could be reduced to a level lower than 0.01 wt%. Equilibrium and kinetic data are presented in this paper. An attempt has been made to correlate the experimental kinetic data with the help of a model for transport in a biporous solid.

EXPERIMENTAL

Materials

Type 4A (IPCL Catad Division, 1.6 mm cylindrical) molecular sieve pellets were used. An aqueous solution of isopropyl alcohol was prepared from distilled water and analytical grade isopropyl alcohol (Glaxo India Ltd.). The concentration of water was measured with a Mettler Karl-Fischer Titrator (DL18 Model). The molecular sieve pellets were dehydrated before use. The pellets were activated at 300°C in vacuum for 6 hours and stored in a desiccator.

Equilibrium Studies

The equilibrium studies were carried out in a specially designed glass cell with a high vacuum stopcock and a silicon rubber septum for liquid sample injection. A known amount of molecular sieve (2–5 g) was taken in the cell and activated for 6 hours at 300°C in vacuum. The cell was allowed to cool to ambient temperature with the vacuum on. After cooling, a liquid mixture (5–6 g) of known composition was injected into the cell through the septum and allowed to equilibrate with occasional shaking in a constant temperature bath for 24 hours. The supernatant solution was analyzed for its water content.

The amount of water adsorbed by the molecular sieves was calculated by mass balance. Equilibrium data were obtained in the 20 to 70°C temperature range at fluid phase concentrations from 0.02 to 9.2 wt% of water. The adsorption data are presented in Fig. 1.

Batch Kinetic Studies

A known amount of molecular sieve was activated at 300°C for 6 hours under vacuum in order to remove any trace of water or other contaminants. The pellets were cooled to ambient temperature, as in the case of

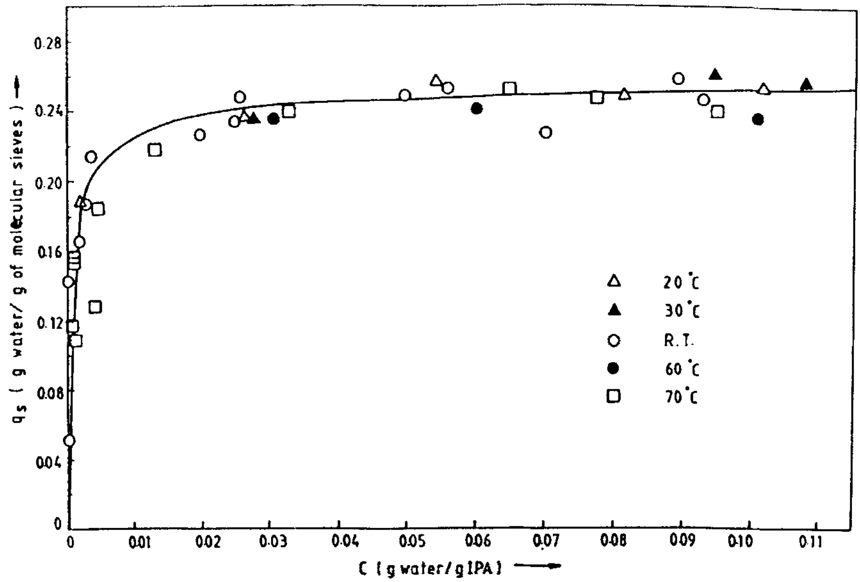

FIG. 1 Experimental equilibrium data for adsorption of water on molecular sieve 4A.

equilibrium studies, and transferred to an adsorption vessel (round bottom flask) and immediately stoppered. Batch kinetics experiments were carried out at room temperature. 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 set sufficiently high to minimize the external mass transfer resistance in Run 1. The speed of the shaker was further increased in Run 2 to check the effect of agitation. Experimental observations in both runs were nearly the same (Fig. 2), thus indicating that the effect of agitation had been minimized. 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 run to determine the final equilibrium composition. The initial concentration of water was varied in Runs 3, 4, and 5. The experimental conditions of the batch runs are summarized in Table 1.

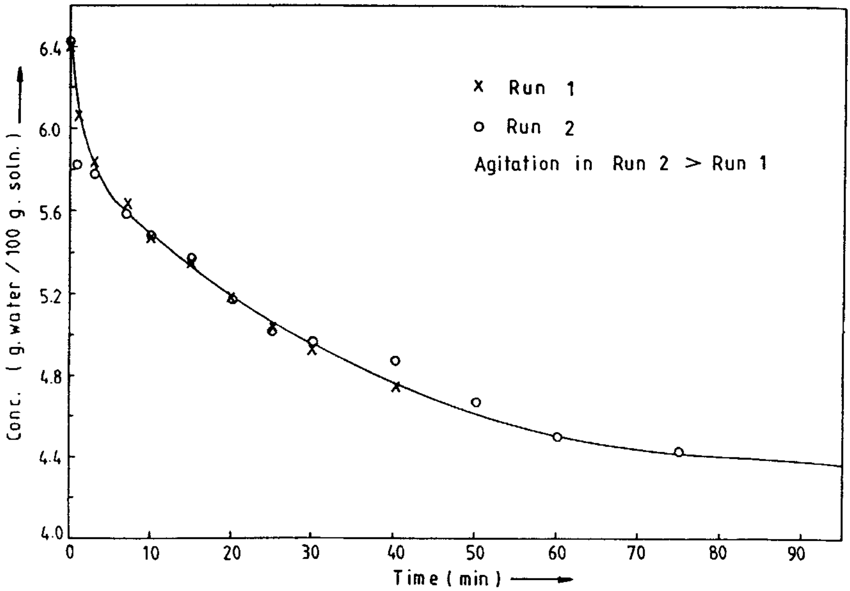

FIG. 2 Kinetics of adsorption: variation of concentration with time.

TABLE 1

Run	Initial concentration (g/100 g)	Final concentration (g/100 g)	Adsorbent (g)	λ
1	6.014	3.86	13.726	0.391
2	6.014	3.87	13.731	0.393
3	3.007	0.91	13.657	0.711
4	1.534	0.095	13.675	1.508
5	7.546	5.43	13.693	0.318

Development of Kinetic Model

An idealized macroporous cylindrical pellet would be composed of an assemblage of small uniform spherical microporous crystals (or microspheres). Macropores are assumed to exist in between the microspheres. Transport within both macropores and microspheres is assumed to occur by Fickian diffusion with coefficients D_p and D_c, respectively, independent of sorbate concentration.

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

At all points within the macropores, equilibrium between the fluid and at the surface of the adjacent microparticles is assumed to be established rapidly, and adsorption on microspheres takes place. The bulk fluid phase concentration of the sorbate decreases with time.

For mathematical simplicity, diffusion through both flat ends of the cylindrical particle is neglected. (The total surface area of the flat ends is only about 8% of the curved area of a cylindrical pellet.)

The kinetics of adsorption is described by the set of Eqs. (1)–(3):

Mass balance equation for macropores in a cylindrical pellet:

$$\epsilon \frac{D_p}{R} \frac{\partial}{\partial R}\left[R \frac{\partial C}{\partial R}\right] = \epsilon \frac{\partial C}{\partial t} + (1 - \epsilon) \frac{\partial \bar{q}}{\partial t} \tag{1}$$

$$\text{I.C.} = C(R, 0) = 0, \qquad q(r, 0) = 0 \text{ for all } R$$

$$\text{B.C. for } t > 0,\ C(R_p, t) = C_0[1 - \lambda U(t)], \qquad \frac{\partial C}{\partial R}[0, t] = 0$$

$$q(r_c, t) = q_0 \text{ when } C(R, t) > 0, \qquad \frac{\partial q}{\partial r}[0, t] = 0$$

Mass balance equation for a microsphere at any position R:

$$\frac{D_c}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q}{\partial r}\right) = \frac{\partial q}{\partial t} \tag{2}$$

$$\overline{q} = \frac{3}{r_c^3}\int_0^{r_c} qr^2\,dr \tag{3}$$

where $\overline{q}$ is the adsorbed phase concentration averaged over a microsphere.

The entire sorption capacity lies in the microspheres only, i.e.,

$$U(t) = 2\int_0^{R_p}\frac{R\overline{q}}{R_p^2 q_0}\,dR \tag{4}$$

where $U(t)$ is the fractional saturation.

In order to solve the above equations numerically, it is convenient to express the equations in terms of the following dimensionless variables.

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

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

Material balance equations in dimensionless form are

$$\frac{1}{\alpha}\left(\frac{\partial^2\theta_p}{\partial\eta^2}\right) + \frac{1}{\alpha\eta}\left(\frac{\partial\theta_p}{\partial\eta}\right) = \frac{\partial\theta_p}{\partial\tau} + \frac{\beta}{3\alpha}\left(\frac{\partial\overline{\theta}_c}{\partial\tau}\right) \tag{5}$$

$$\text{I.C.: } \theta_p(\eta, 0) = 0, \qquad \theta_c(\gamma, 0) = 0 \text{ for all } \eta$$

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

where $\lambda = mq_s/V_l C_0$.

$$\frac{\partial}{\partial\gamma}\left(\gamma^2\frac{\partial\theta_c}{\partial\gamma}\right) = \frac{\partial\theta_c}{\partial\tau} \tag{6a}$$

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

The fractional saturation for a microsphere is given by

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

$$U(\tau) = 2\int_0^1 \overline{\theta}_c(\eta, \tau)\eta\,d\eta \tag{7}$$

The set of Eqs. (5)–(7) was solved numerically by the explicit forward difference method. A computer program was developed to generate a concentration profile in macropores and fractional saturation of the entire pellet, Eq. (7). The correctness of the computer program was established by comparing the dimensionless concentration profile in macropores for a nonadsorbing pellet, obtained numerically, and that obtained by an analytical method (22).

RESULTS AND DISCUSSION

Equilibrium Data

The equilibrium data for water–isopropyl alcohol and 4A molecular sieve at various temperatures are shown in Fig. 1. Except at very low concentrations of water (say up to 0.002) the grams of water sorbed per gram of dry molecular sieves is around 0.25. Breck (7) reported the capacity of 4A molecular sieve for water to be up to 0.25 g water per gram of dry adsorbent. It was also observed by the authors that 1 g of dry molecular sieve could pick up 0.25 g of moisture from the atmospheric air. This corresponds to 0.29 g/cm^3 of the cylindrical pellet.

The rectangular type of isotherm behavior shown by molecular sieves is due to the strong ionic interaction of cations in the structure of molecular sieve crystals with water molecules. When the micropores in the crystals are filled, further adsorption does not take place.

Batch Kinetics

As indicated earlier, 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 with the help of sorption at a given time and the corresponding equilibrium value.

Figure 2 shows that there is no change in rate of sorption with agitation. All experiments were carried out at the higher agitation. The kinetic results of Run 2 are given in Fig. 3. It shows fractional saturation. It is observed that water uptake is rapid initially and decreases later. A similar trend is observed in Fig. 4 which shows the consolidated plots of other batch kinetic runs with different initial concentrations. As expected, the rate of sorption increases with an increase in concentration.

Correlation of Experimental Data

The correlation of computed results with experimental data has been carried out. From Eq. (5) it is observed that the following parameters need to be defined before performing computations: C_0, ϵ, D_p and R_p, q_0, D_c and R_c. Experimental value of C_0, $(1 - \epsilon)q_0$, and R_p are known

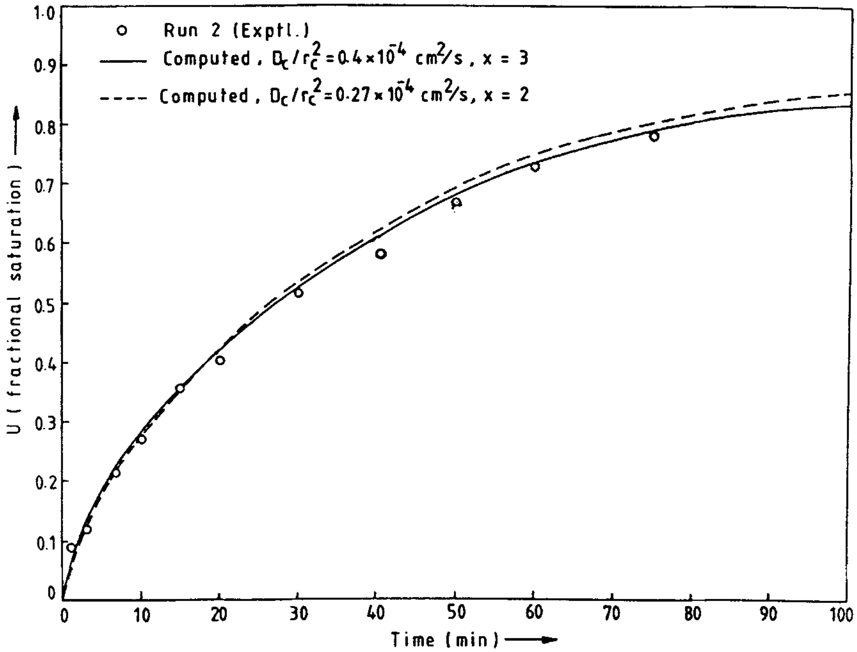

FIG. 3 Kinetics of adsorption: variation of fractional saturation with time.

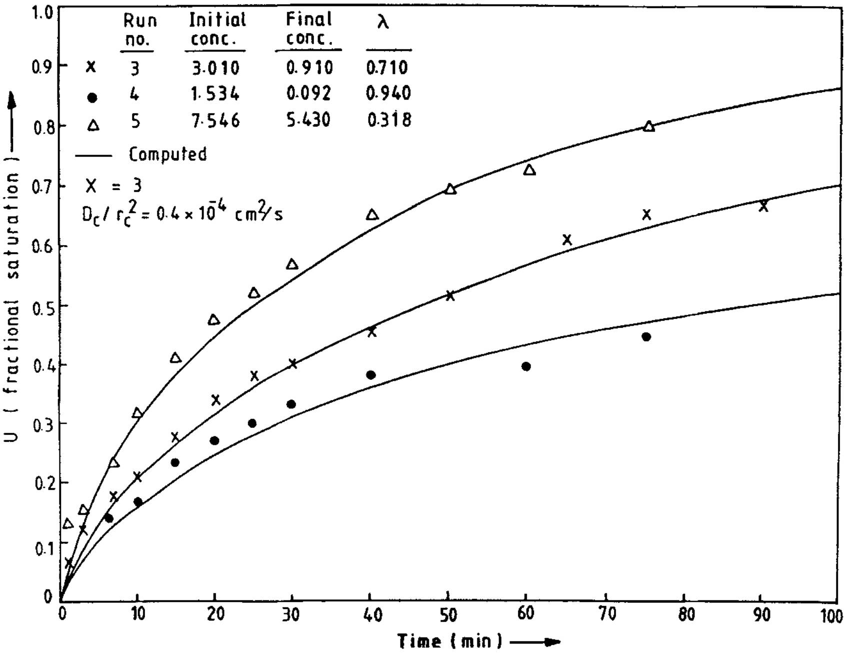

FIG. 4 Kinetics of adsorption: comparison of experimental and computed results.

independently. Whereas ϵ and q_0 are not known independently, the sorption capacity of the pellet, $(1 - \epsilon)q_0$, is experimentally determinable.

The macropore diffusion coefficient may be estimated (23) as

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

where X is the tortuosity factor (an empirical constant characterizing both the shape and orientation of the pores). D_m is the molecular diffusion coefficient of the adsorbate in the bulk fluid phase.

The above equation is used for estimating D_p for the following reasons: 1) its dependence on porosity is most important because porosity does not change during adsorption or desorption, and 2) the obtained empirical values of X reported in the literature are based on this equation. The reported value of X for zeolites is 1.7–4.5 (24). Lee and Ruthven (25) reported a value of 2.0 for 5A molecular sieves, but a value of 3.3 has also been reported (26). A value of 3 has been assumed in the present system. The value for porosity in the present study has been taken as 0.35 for 4A molecular sieves. Nearly the same value has been reported in the literature for different molecular sieves. Teo and Ruthven (4) used 0.33 for the 3A molecular sieve, Kyte (27) reported 0.34 for the 4A molecular sieve, and Suzuki (26) gave 0.32 for the 5A molecular sieve.

Now, for generating a theoretical uptake curve, all the parameters are known except D_c/r_c^2, which was determined by matching computed results with experimental data. The value of D_c/r_c^2 was found to be 0.4×10^{-4} cm^2/s for Run 2, and this same value was used for all the experimental runs. The parameters D_p and D_c/r_c^2 cannot be determined independently in the present situation. It is quite likely that there is more than one pair of values of D_p and D_c/r_c^2 which would correlate with the given set of data.

Another set of tortuosity and D_c/r_c^2 values was also tried for matching computed results with experimental data for Run 2: 2 and 0.27×10^{-4}, respectively (Fig. 3). It appears that the first pair gives a slightly better correlation, and the same pair could also be successfully used for matching data for all runs, i.e., tortuosity value as 3 and 0.4×10^{-4} for D_c/R_c^2 (Fig. 4). The same pair also could be successfully used for correlating experimental data for sorption of moisture from atmospheric air on the 4A molecular sieve. It may be possible that another pair of values would correlate the data slightly better than what has been achieved. However, the uniqueness of the values of the parameters cannot be ascertained independently.

CONCLUSION

The feasibility of drying of isopropyl alcohol with 4A type molecular sieve has been demonstrated. It has been shown that its water-holding capacity is 0.25 g per gram of dry molecular sieve, and the equilibrium isotherm is almost rectangular in shape. Experimental kinetic data could be successfully correlated by a mathematical model incorporating diffusion in macropores and microspheres for an assumed rectangular equilibrium. Assuming a value of macroporosity as 0.35 and tortuosity as 3, the value of D_c/r_c^2 was determined to be 0.4×10^{-4} cm^2/s.

NOMENCLATURE

B.C.	boundary condition
C	liquid phase concentration of water at any radial position R (g/cm^3 of liquid mixture)
C_0	initial concentration of water in bulk fluid phase (g/cm^3)
D_c	microsphere diffusivity (cm^2·s^{-1})
D_m	molecular diffusivity of the adsorbate in the bulk fluid phase (cm^2·s^{-1})
D_p	macropore diffusivity (cm^2·s^{-1})
I.C.	initial condition
m	mass of adsorbent (g)
q	concentration of sorbate at any radial position, r in the microsphere (g/cm^3) of solid phase)
$\overline{q}$	concentration of sorbate averaged over a microsphere
q_0	adsorbent capacity (g/cm^3 of microsphere volume)
q_s	adsorption capacity (g/g of adsorbent)
q_p	adsorption capacity (g/cm^3 of adsorbent pellet volume), $(1 - \epsilon)q_0$
r	radial coordinate (microsphere)
r_c	microsphere radius (cm)
R	radial coordinate (macropore)
R_p	radius of cylindrical pellet (cm)
t	time (s)
U	fractional saturation of adsorbent
V_l	volume of liquid mixture (cm^3)
X	tortuosity factor

Greek Symbols

α	$D_cR_p^2/D_pr_c^2$, ratio of diffusional time constants
β	$3\,(1 - \epsilon)q_0\alpha/\epsilon C_0$, dimensionless diffusion parameter
γ	r/r_c, dimensionless microsphere radius
η	R/R_p, dimensionless macropore radius
τ	tD_c/r_c^2, dimensionless time

θ_p	C/C_0, dimensionless concentration in macropore
θ_c	q/q_0, fractional saturation in microsphere
$\bar{\theta}_c$	fractional saturation averaged over a microsphere at any η
ϵ	voidage of pellet
λ	ratio of sorption capacity of the adsorbent and total adsorbate initially present in solution

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Received by editor October 4, 1993