Mass Transfer of CFC-113 in Adsorption Bed with Silica Gel Spheres

Sung-Yong Cho

CFC Center, KIST
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구형 실리카겔이 충전된 흡착탑에서의 CFC-113의 물질전달
조성용

한국과학기술연구원 CFC센터
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Abstract: Adsorption experiments of 1,1,2-trichloro-2,2,1-trifluoroethane(CFC-113) on silica gel were carried out isothermally and effective overall mass transfer coefficients based on linear driving force model were evaluated. This article focuses on the adsorption capacity and the effective overall mass transfer coefficient, in order to assist the design of fixed adsorption bed. The effects of CFC-113 concentration in air on effective overall mass transfer coefficient at 298K were studied. A linear driving force model was found to provide a good fit to the experimental data obtained from the low concentration ranges.

요약: 구형 실리카겔에 대한 1,1,2-trichloro-2,2,1-trifluoroethane(CFC-113)의 흡착 실험을 동반 하여 수행하여 Linear Driving Force(LDF)모델을 사용하여 유호 총괄 물질 계수(Effective Overall Mass Transfer Coefficient)를 구하였다. 본 연구는 고정층 흡착탑 설계에서 중요한 인자인 평형 흡착량과 유호 총괄 물질 전달 계수를 고찰하였으며 298K에서 CFC-113의 탑 내주일 녹도가 유호 총괄 물질 전달 계수에 미치는 영향을 고찰하였다. 또한 LDF모델에 의한 전산 모사 결과를 사용하여 본 연구에서 얻어진 실험 결과를 잘 설명할 수 있었다.

1. Introduction

In general, gas phase adsorptions include gas dehydration, removal of pollutants from atmospheric emissions, and detoxification of ventilation air. These all have in common large volumes of gas and low impurity level. The adsorption technologies for removing and recovering organic solvents have been attracting special interests in the aspects of protecting the environment from pollution and saving the cost[1, 2].

Particularly, some reports suggested that CFC-113 released to the atmosphere may deplete the stratospheric ozone layer[3, 4].

Therefore, emissions of CFC-113, which has been widely used as a solvent to clean electronic assemblies, to the atmosphere are limited by regulations and adsorption operation is focused as one of the important techniques for removal and recovery of CFC-113[2].
The present study include the equilibrium capacity and the effective overall mass transfer coefficient of 1,1,2-trichloro-2,2,1-trifluoroethane in fixed bed with silica gel spheres at 298K, in order to assist the design of the adsorption facilities.

2. Experiment

A conventional apparatus was used for the measurement of adsorption equilibrium at 298K and an automatic sorption analyzer (model: Autosorb 1) was used for characterization of the adsorbent[5].

A fixed bed unit was used to study adsorption of CFC-113 on silica gel. A schematic diagram of the fixed bed unit is shown in Fig. 1. Dry air was used as the carrier gas during the adsorption operation. The flow rate of air was measured and digitally displayed by an electronic mass flow meter (Floline, model no. SEF-11). The saturated vapor of CFC-113 was elevated and carried by a branch stream of air through the graduated pressure bottle in a thermostat. This stream was then mixed with the pure air stream. The adsorption bed was fabricated from 5.0cm I.D. stainless steel pipe. The bed was about 40cm long and was packed to 33cm height with silica gel. Before packing, the adsorbent was dried in a vacuum oven. In order to support the adsorbent and uniform gas distribution, two knit mesh were placed at top and bottom of the bed. Three thermocouples were installed at top, middle, and bottom of the bed to monitor the temperatures of bed. This fixed bed was placed in air bath, in order to maintain the 298K. The inlet and effluent gas were continuously detected and recorded by the infrared analyzer (Riken model RI-413A) calibrated by standard gas.

Silica gel spheres, supplied by DOHKAI Chemical Industry Co. Ltd., were employed as an adsorbent. The physical properties and SEM (Scanning Electron Microscopy) of this adsorbent are listed in Table 1 and Fig. 2, respectively. 1,1,2-trichloro-2,2,1-trifluoroethane(CFC-113) was employed as an adsorbate supplied by Daikan company.

3. Theoretical Review

One way to describe the characteristics of fixed bed is examining the concentration vs. time curves (breakthrough curves) of the effluent. These breakthrough curves are perhaps the most common basis for assessing the behavior of adsorber.

In this study, the system pressure, system temper-

Table 1. Physical Properties of the Adsorbent

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Silica gel sphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Density</td>
<td>462</td>
</tr>
<tr>
<td>(kg/m³ bed)</td>
<td></td>
</tr>
<tr>
<td>Geometric Area</td>
<td>19.08</td>
</tr>
<tr>
<td>a: (1/cm)</td>
<td></td>
</tr>
<tr>
<td>Equivalent diameter</td>
<td>3.18</td>
</tr>
<tr>
<td>dₜ: (mm)</td>
<td></td>
</tr>
<tr>
<td>BET Surface Area*</td>
<td>618</td>
</tr>
<tr>
<td>(m²/g)</td>
<td></td>
</tr>
<tr>
<td>Void in Packed Bed</td>
<td>0.32</td>
</tr>
<tr>
<td>(cm³/cm³)</td>
<td></td>
</tr>
<tr>
<td>Mean Pore Diameter**</td>
<td>93.7</td>
</tr>
<tr>
<td>(nm)</td>
<td></td>
</tr>
</tbody>
</table>

* from nitrogen adsorption at 77K(0.162nm²/molecule).
** by the automatic sorption analyzer.
Fig. 2. The scanning electron microscopy of silica gel sphere.

ature, carrier gas flow rate, and feed concentration are assumed to be constant and controlled within 3 ~8% error. Also, the gas phase is assumed to obey the ideal gas behavior. Radial temperature, concentration and velocity gradient within the bed are neglected. Accumulation of carrier gas in the pores of the solid phase is disregarded. The amount of carrier gas adsorbed is negligible and the adsorbent can be modeled as spheres.

Based on the assumptions made above, a complete dynamic model of a fixed-bed adsorber could be developed as follows:

\[ \mu \cdot \left( \frac{\partial C}{\partial x} \right)_{y} + \rho \cdot \left( \frac{\partial W}{\partial x} \right)_{y} + \epsilon \cdot \left( \frac{\partial C}{\partial y} \right)_{x} = D_{i} \cdot \left( \frac{\partial^{2} C}{\partial z^{2}} \right) \]

(1)

With boundary conditions

\[ C(0, t) = C, \]
\[ W(Z, 0) = 0 \]

(2)

\[ W^{*} = f(T, C) \]  \hspace{1cm} (3)

We have also neglected the effect of longitudinal diffusion term, \( D_{i} \left( \frac{\partial^{2} C}{\partial Z^{2}} \right) \), on the right-hand side of equation (1).

Furthermore, if the isotherm is linear, the equation (3) becomes as follows:

\[ W^{*} / C = \beta \]  \hspace{1cm} (4)

Substitution of equation (2) and (4) into (1) gives an analytical solution which is analogous to that of Anzelius[6] were derived for the heat transfer problem using the Laplace transformation method.

\[ \frac{C}{C} = e^{-\left( x + y \right)} \cdot I_{0} \left( 2 \sqrt{XY} \right) + \sum_{n=1}^{\infty} \left( e^{-n^{2} \beta x} \cdot I_{0}(2 \sqrt{XY}) \right) dY \]  \hspace{1cm} (5)

Where

\[ X = K_{eff} \cdot a_{e} (Z / u) \]
\[ Y = K_{eff} \cdot a_{e} \left( t / (\beta \sigma) \right) \]

Although the expressions for the breakthrough curve derived from the various models are algebraically different[6, 7], the numerical differences are quite small. Equation (5) numerically evaluated and obtained optimum overall mass transfer coefficient from computer simulation.

In bed operation, adsorbates initially transfer from the bulk gas through an external film and to the external surface of the particle. Molecules of the adsorbates diffuse into the particle, are adsorbed on active sites, and then diffuse along the surface. Film transfer and pore diffusion are treated as sequential steps, but pore diffusion and surface diffusion generally take place in parallel. Any combination of the resulting three steps can constitute the rate-controlling mechanism. This combination varies with adsorbate-adsorbent system and can even change with operating conditions for a given system[8]. When the surface adhesion step is essentially instantaneous, the gas in the pores is at local equilibrium with the solid phase. Therefore, the effective overall mass transfer coefficient is expressed as follows [8]:

\[ \frac{1}{K_{eff}} = \frac{1}{k} + \frac{R}{5 \cdot D_{i} \cdot \epsilon_{s}} \]  \hspace{1cm} (6)
Several empirical correlations for the coefficient, \( k_m \), are available, but that of Petrovic and Thodos [9] was chosen for the present study. The correlation is expressed as follows:

\[
k_m = \frac{0.357}{d_p^{\alpha}} \cdot Re^{\beta} \cdot Sc^{\gamma} \cdot \left( \frac{D_v}{d_p} \right); \quad 3<Re<2000
\]  

(7)

The pore and surface diffusion coefficients can be related with the equilibrium equation and combined into an effective diffusion coefficient.

\[
D_e = D_x + D_y \cdot \frac{2W^{*}}{\beta e}
\]  

(8)

In equation (8), pore diffusion includes both molecular and Knudsen diffusion. When both Knudsen and molecular diffusion contribute to the flux through the pores, a combined coefficient can be defined as follows[10].

\[
\frac{1}{D_k} = \frac{(1-y)}{D_w} + \frac{1}{D_{kn}}
\]  

(9)

3. Results and Discussion

Fig. 3 shows the equilibrium amount of 1,1,2-trichloro-2,2,1-trifluoroethane on silica gel at 298K. From this figure, it is found that the isotherm of 1,1,2-trichloro-2,2,1-trifluoroethane on silica gel is nearly linear in low concentration ranges and this result is similar to Kodama’s report[2]. Therefore, the adsorption equilibrium constant, \( \beta \), is determined as 48.

Fig. 4 shows the comparable plot of calculated curves by equation (5) with experimental data. The shapes of the breakthrough fronts are observed to slight changes with the variations of inlet concentration.

Fig. 5 shows the effective overall mass transfer coefficient in fixed adsorption bed with silica gel spheres. The effective overall mass transfer coefficient of 1,1,2-trichloro-...
2,2,1-trifluoroethane on silica gel spheres in fixed adsorption bed is slightly decreased with increase of inlet concentration. It suggest that the mass transfer resistance in low concentration is less than that in high concentration. In equation (6), the overall mass transfer resistance is composed of fluid film resistance and solid resistance. In order to calculate the overall mass transfer resistance, the molecular diffusion coefficient, $D_m$, is estimated by the Gilliland equation[11].

$$D_m = 0.2854 \times 10^{-1} \times T^{0.7}/P$$  \hspace{1cm} (10)

Employing this equation, the molecular diffusion coefficient for the CFC-113-air system is 0.0607 cm$^2$/s at 1 atm and 298K (c.f. $D_m$ of CFC-112 was 0.0647 cm$/s$ at 1 atm and 298K[12]).

Furthermore, the Knudsen diffusion coefficient is estimated by the following equation[13].

$$D_{ko} = 7.981 \times 10^{-4} \cdot \left( \frac{Z}{T} \right) \left( \frac{T}{M} \right)^{1/2}$$  \hspace{1cm} (11)

From the measurement by the automatic sorption analyzer, the pore radius is about 4.8 angstroms for this silica gel sphere.

With a pore tortuosity factor of four[10], $D_{ko}$ is approximately 0.000146 cm$^2$/s at 298K. As a result, since $D_m$ is about two orders of magnitude greater than $D_{ko}$ for the system of interest. Hence, is equation (9), $D_k$ is nearly $D_{ko}$ and contribution of $D_m$ is neglected.

Fig. 6 shows the ratio of the film resistance to the overall resistance. In this figure, it was found that the film resistance is very smaller than the overall resistance. It means that the solid diffusion is rate-controlling mechanism in this system.

Therefore, when the surface adhesion step is essentially instantaneous, the surface diffusivity, $D_s$, is of interest.

Using the equation (8), the estimated surface diffusivities of CFC-113 on silica gel sphere with the variation of inlet concentration are depicted in Fig. 7.

In Fig. 7, when the bed inlet concentration is increased, the surface diffusivity is nearly constant ($0.8 \times 10^{-3} \text{cm}^2/\text{s}$).

These results are slightly higher than Kodama's results that were obtained from the carbon adsorption ($0.2-0.9 \times 10^{-3} \text{cm}^2/\text{s}$)[2].

4. Conclusions

The adsorption isotherm of 1,1,2-trichloro-2,2,1-
trifluoroethane on silica gel sphere was measured at 298K. This isotherm was found to be linear.

The fixed bed experiments were carried out and overall mass transfer coefficients were evaluated by the computer simulation. In this system, the solid diffusion is the rate controlling step of mass transfer mechanism. Using the Linear Driving Force (LDF) model, the surface diffusivities of the 1,1,2-trichloro-2,2,1-trifluoroethane on the silica gel sphere were estimated. It is expected that these values can be used to design the adsorption facilities.

Nomenclature

\[ \theta \] dimensionless time
\[ \beta \] adsorption equilibrium constant\([\text{m}^2/\text{m}^3]\)
\[ \rho \] gas density\([\text{kg}/\text{m}^3]\)
\[ \rho_s \] particle density\([\text{kg}/\text{m}^3]\)
\[ \rho_c \] solute density\([\text{kg}/\text{m}^3]\)
\[ \gamma \] bulk density\([\text{kg}/\text{m}^3]\)
\[ \varepsilon_a \] external voidage
\[ \varepsilon_p \] particle voidage
\[ \mu \] gas viscosity\([\text{kg}/\text{m} \cdot \text{s}]\)
\[ r_e \] mean pore radius\([\text{cm}]\)
\[ r_t \] particle tortuosity

\[ \text{Re} \] Reynolds number\([\alpha_d \mu/\mu]\)
\[ \text{Sc} \] Schmidt number\([\mu/(\rho \cdot D_m)]\)

References

10. C. N. Scatterfield, “Mass Transfer in Heterogeneous Catalysis”, MIT Press, Cam-
