Table 1. Apparent activation energies for permeation and diffusion of some gases through cellulose acetate dense membrane

<table>
<thead>
<tr>
<th>Gases</th>
<th>$E_p$ [KJ/mol]</th>
<th>$E_d$ [KJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>14.8</td>
<td>14.4</td>
</tr>
<tr>
<td>He</td>
<td>20.7</td>
<td>40.9</td>
</tr>
<tr>
<td>CH₄</td>
<td>21.5</td>
<td>40.6</td>
</tr>
<tr>
<td>N₂</td>
<td>19.7</td>
<td>36.9</td>
</tr>
<tr>
<td>CO</td>
<td>16.2</td>
<td>34.0</td>
</tr>
<tr>
<td>O₂</td>
<td>20.8</td>
<td>38.1</td>
</tr>
<tr>
<td>Ar</td>
<td>8.95</td>
<td>32.4</td>
</tr>
<tr>
<td>CO₂</td>
<td>30.0</td>
<td>51.9</td>
</tr>
</tbody>
</table>

membrane preparation process.

Acknowledgement

This work is a part of the results of "C. Chemistry Project," a National Research and Development Program of the Agency of Industrial Science and Technology, Ministry of International Trade and Industry (M.I.T.I.), Japan.

Nomenclature

$D_p = \text{apparent diffusion coefficient calculated from Eq. (1)}$ [m²·s⁻¹]

$E_p = \text{apparent activation energy for permeation}$ [KJ·mol⁻¹]

$E_d = \text{apparent activation energy for diffusion}$ [KJ·mol⁻¹]

$l = \text{membrane thickness}$ [m]

$P = \text{apparent permeability coefficient}$ [m³(STP)·m⁻²·s⁻¹·Pa⁻¹]

$\theta = \text{time lag}$ [s]

Literature Cited


DYNAMIC DRYING OF BENZENE WITH ION-EXCHANGE RESIN

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Key Words: Adsorption, Desorption, Drying, Isotherm, Ion Exchange Resin, Moisture, Benzene

Various organic solutions are used in many industries such as the petrochemical industry. The presence of moisture in those solvents results in poor insulation, corrosion of apparatus and catalyst poisoning. Therefore, the moisture content of the solvents must be reduced to less than several ppm.

Since ion exchange resins have an ability to adsorb selectively polar substances from nonpolar solvents, they have been used for the drying of organic solvents. In the previous paper, a cation-exchange resin was shown to be excellent in the drying of nonpolar solvent such as benzene, and its capacity to adsorb water varied greatly with temperature.

In this study, periodic adsorption and desorption were investigated to utilize the great temperature dependency and the reversibility of adsorption equilibria of the resin-water system. A tapered column was used to reduce the pressure drop due to expansion of the resin.

1. Principle of Adsorption and Desorption Process

Adsorption isotherms are always linear and there are significant differences of adsorption capacity between 283 K and 333 K. The solubilities of water in benzene are 0.396 and 1.44 kg/m³ at 283 K and 333 K.
Therefore, it is feasible to use this difference to remove water from benzene.

The schematic diagram of the drying system is shown in Fig. 1. A feed solvent and an effluent from a desorption column are mixed and cooled in a settler. Since the concentration of water is higher than the solubility, a water phase can be separated and removed from a solvent phase. The saturated solvent flows through the adsorption column kept at lower temperature until the concentration of water reaches the breakthrough point. Solvent dried to nearly zero concentration of water can be obtained. The exhausted column may be regenerated by increasing the temperature of the column. The dried solvent passes through the column kept at higher temperature until the concentration of water attains the end point of the breakthrough curve.

Therefore, solvent dried in one cycle can be obtained by subtracting the volume obtained in the desorption process from that in the adsorption process.

2. Experimental

2.1 Adsorbent

A strongly acidic cation exchange resin, Dowex 50W-X8, which was essentially identical to the Dowex HCR-S described in the previous paper, was used as an adsorbent. Portions of average particle diameter 0.115 and 0.324 mm were used.

2.2 Experimental apparatus and procedure

Feed solution was prepared to obtain the required concentration by adding distilled water to dried benzene. Feed solution was introduced to the bottom of the adsorption column through a flow control valve, a rotameter and a heat exchanger. Both adsorption and desorption were carried out in up flow and samples for analysis were taken at the top of the column with a syringe. The column and the heat exchanger were maintained at 283 K for adsorption and at 333 K for desorption. The pressure drop in the bed was measured by a mercury manometer. The volume of the resin bed increased with adsorption of water and finally showed about 30% increase in volume. Therefore, the pressure drop increased rapidly in a fixed bed packed with small particles and it was difficult for the solution to flow through the column. This problem was solved by using a tapered fixed-bed column with a slightly conical shape. Namely, the fixed-bed column was changed to a tapered glass tube of 7.0 mm average i.d. The angle of the taper was 0.015 radian and the bed height was 30 mm. Adsorption and desorption operations were repeated for the same column.

The moisture concentration in benzene was measured by a Karl-Fisher moisture meter.

3. Results and Discussion

3.1 Adsorption isotherms

Figure 2 shows adsorption isotherms of water in benzene for cation-exchange resin, Dowex 50W-X8 in the Na⁺ and H⁺ forms at 283 K and 333 K. The adsorption isotherms are represented by linear relations. Adsorption capacities are significantly different between 283 K and 333 K. Adsorption capacity of the resin in the H⁺ form is greater than that in the Na⁺ form. However, since the resin in the H⁺ form was unstable in benzene, that in the Na⁺ form was adopted for the work described in the following sections.

3.2 Pressure drop in the fixed bed

Figure 3 shows the pressure drop in the fixed bed of both straight and tapered column during adsorption. The average diameter of the resin, \(d_p\), was 1.15 \(10^{-4}\) m and the amount, \(W\), was 1.06 \(10^{-3}\) kg. The flow rate, \(u\), was 3.0 \(10^{-3}\) m/s and the initial length of the bed was about 3.0 \(10^{-2}\) m. In the case of the tapered column, the bed expanded easily in the axial direction and the pressure drop did not increase greatly.

3.3 Adsorption and desorption in the tapered column

Figure 4 shows results for the tapered fixed bed. The water concentration of feed solution to the column, \(C_0\), was 0.22 kg/m³. The desorption curve was obtained by operating with benzene at a water concentration of 0.0415 kg/m³ at 333 K. The ordinate of this figure indicates \(C/C_0\) for adsorption and \(K_d C/(K_H C_0)\) for desorption since the maximum concentration in the desorption process was \(K_0 C_0/K_H\). The influences of water concentrations of feed solution, particle sizes, and flow rates were examined for the tapered fixed bed as shown in Figs. 5–7.

3.4 Calculated breakthrough curves

Theoretical breakthrough curves in the case of a linear isotherm were calculated by an analytical solution, taking account of axial dispersion and resistances of intraparticle diffusion and mass transfer from liquid to solid. Although liquid velocity in the tapered column decreased along the axial direction by
about 20%, constant velocity was assumed for simplicity of calculation.

The liquid-solid mass transfer coefficient was estimated by the correlation of Dwivedi et al.\textsuperscript{1)} The intraparticle diffusivity was obtained from batch adsorption measurements ($D_s = 3.0 \times 10^{-12}$ m$^2$/s at 283 K and $D_s = 7.0 \times 10^{-12}$ m$^2$/s at 333 K). The values of adsorption equilibrium constant and axial dispersion coefficient were determined by curve fitting. The
adsorption equilibrium constant obtained 
(K = 0.85 m³/kg) was a little smaller than that from
the adsorption isotherm (0.896 m³/kg). The axial disper-
sion coefficient was approximated by \( D_L = 1.1 \times 10^{-3} \text{m}^2/\text{s} \). The solid lines in Figs. 4-7 indicate the
calculated results.

The breakthrough curves are almost independent
of feed concentration, as shown in Fig. 5. This result
could be predicted from the fact that the adsorption
isotherm was linear. The breakthrough curve is
steeper for smaller-size resin, as shown in Fig. 6.
Then the intraparticle diffusion resistance became
significant for the larger-size resin. The effect of
flow rate is shown in Fig. 7. The curve is steeper for
lower flow rates.

The desorption curve was also calculated and is
shown in Fig. 4. The parameters were determined as
\( K = 0.229 \text{m}^3/\text{kg} \) and \( D_L = 7.1 \times 10^{-3} \text{m}^2/\text{s} \).

Nomenclature

\( C \) = water concentration in solvent \([\text{kg/m}^3]\)

\( C_0 \) = influent or initial water concentration \([\text{kg/m}^3]\)

\( D_L \) = axial dispersion coefficient \([\text{m}^3/\text{s}]\)

\( D_s \) = effective surface diffusivity \([\text{m}^3/\text{s}]\)

\( d_p \) = particle diameter \([\text{m}]\)

\( K \) = adsorption equilibrium constant \([\text{m}^3/\text{kg}]\)

\( \Delta P \) = pressure drop \([\text{Pa}]\)

\( Q \) = effluent volume \([\text{m}^3]\)

\( q \) = amount adsorbed within a particle \([-]\)

\( u \) = superficial fluid velocity \([\text{m/s}]\)

\( W \) = weight of adsorbent particles \([\text{kg}]\)

\( \langle \text{Subscripts} \rangle \)

\( H \) = higher temperature (333 K) \([\text{K}]\)

\( L \) = lower temperature (283 K) \([\text{K}]\)

Literature Cited

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EFFECT OF FACILITATED DIFFUSION IN INTERNAL
AQUEOUS DROPLETS ON EFFECTIVE DIFFUSIVITY
AND EXTRACTION RATE OF PHENOL IN
EMULSION LIQUID MEMBRANES

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Key Words: Emulsion Liquid Membrane, Facilitated Transport, Effective Diffusivity, Phenol, Extraction

Although several studies\(^{1,3-5,7,9}\) have been
presented on the mechanism of the permeation of phenol
through emulsion liquid membranes containing aque-
ous sodium hydroxide solutions in the internal dro-
plets, the effective diffusivity in W/O emulsion drops
has not been investigated in detail.

One of the present authors derived an equation of
the effective diffusivity by applying Russel’s model,\(^8\)
which had been proposed for conductive heat transfer
through porous media, to the diffusion of phenol\(^9\)
and amine\(^9\) in W/O emulsion drops, and suggested
the possibility that phenol can be transported in the
forms of phenol and phenolate ion in the internal
aqueous phase. This transport is regarded as a kind of
facilitated transport in which \(\text{OH}^-\) functions as a
carrier of phenol. However, the contribution of the
facilitated diffusion to the total flux through W/O
emulsion phase was not elucidated.

In this work, the equation of effective diffusivity is
derived by taking into account the facilitated dif-
fusion on the basis of Russel’s model.

1. Model Description

The mass transfer model is schematically shown in
Fig. 1. The small cube represents a droplet of the
internal aqueous phase and the large cube an element
which consists of a droplet of the internal aqueous
phase and the membrane which surrounds the drop-