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# REMOVAL OF ACETIC ACID IMPURITIES FROM ETHYL ACETATE BY ADSORPTION ON ION EXCHANGE RESINS

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## ABSTRACT

Removal of acetic acid impurities from ethyl acetate was attempted by sorption on basic ion-exchange resins. Kinetic studies showed that acid removal is controlled by intraparticle resistance from both ethyl acetate and alcohol. Breakthrough curves for uptake of the acid from ethyl acetate were obtained at different flow rates and concentrations. Desorption studies were performed using both ethyl acetate and alcohol. No appreciable resin degradation or loss of capacity was observed even after repeated adsorption-desorption cycles. Experimental equilibrium and kinetic data were used to predict the performance of the adsorption column.

## INTRODUCTION

Removal of acetic acid impurities from ethyl acetate is important in industries where the use of acid-free solvent is required. However, conventional distillation requires a large number of stages and/or high reflux to remove acetic acid

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*Corresponding author. Fax: 91-22-4145614; E-mail: vgg@udct.ernet.in impurities. Neutralization of acetic acid with an alkaline solution is likely to hydrolyze some ethyl acetate and create concomitant emulsification problems. The removal of acidic impurities from ethyl acetate has been reported by researchers who employed several reactive techniques in the recent past. Distillation in the presence of hexamethylene tetraamine or monoethanolamine (1), potassium acetate (2), and sulfuric acid (3) has been reported to give acceptable levels of the acid in distillate. When amines were used in the distillation, impurities formed nonvolatile complexes and were retained in the bottom of the column.

Adsorption on $CaCO_3$ (4) and activated carbon (5) has been employed for purification of ethyl acetate. A simultaneous adsorption of acidic impurities during the removal of diethyl acetal impurities from ethyl acetate was reported to have been achieved when the ester was passed through a column containing 10% sulfonated, strongly acidic resin (6). However, the acidic resin had relatively low adsorption capacity for the acid and the adsorption involved only van der Waals forces. The resin was probably more useful in removing the acetal impurities and moisture from the ester phase than it was in removing the acidic impurities. Reports are also available on the small extent of acetic acid adsorption on acidic resins during liquid-phase esterification catalyzed by a highly cross-linked sulfonic acid resin (7,8).

Adsorption of acetic acid or other acidic impurities on a selective sorbent is a potential technique to purify ethyl acetate. In recent years, we have demonstrated the usefulness of functionalized polymers for adsorption of acetic acid from organic solvents (9) and also for separation of close boiling points phenolic mixtures (10). We have also reported on adsorptive removal of naphthenic acids from organic solvents through the use of ion exchange resins (11). The macroporous weakly anionic resins have a better adsorption capacity for naphthenic acids from petroleum oil than do strong anion-exchange resins with isoporous structures. The functional groups on these resins, if judiciously selected, can impart very high selectivity to the resin. Compared to the applications of ion exchangers in aqueous conditions, the sorption from nonaqueous solutions has received limited attention.

We have reported results of equilibrium batch adsorption of acetic acid from ethyl acetate and ethanol (95%) + water (5%) solutions on polymeric ion-exchange resins (IERs) based on a macroporous styrene-divinylbenzene copolymer matrix with tertiary or quaternary amino groups (9). Very selective adsorption of the acid and high loading capacity were observed for all resins; the resins with tertiary amino groups showed the best selectivity. The adsorption on these resins in organic solutions was reinforced by specific hydrogen-bonding interactions with the functional groups, which resulted in hydrogen bonded complexes. The weakly basic resins carry tertiary amino groups as the functional groups. Because these amino groups do not carry any charge, counter-ion association is negligible and the ion exchange mechanism is not strictly applicable. For functionalized poly-

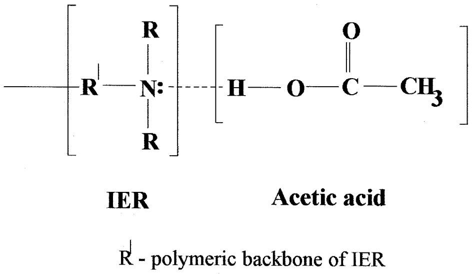

*Figure 1.* Schematic representation of the interaction between the weakly basic resin and acetic acid.

mers of such types, Lewis acid-base interactions in which hydrogen bonds are formed between the lone pair of electrons on nitrogen and acidic hydrogen seem more probable than ion exchange (Fig. 1).

The polymeric structure of the ion exchange resins also swells significantly when brought in contact with organic solvents because the solvent penetrates the polymeric network of the resin phase. The coiled and packed chains of the polymer matrix unfold and make room for the solvent molecules; however, cross-linking does not allow for indefinite accommodation of solvent molecules. The extent of swelling was dependent on the nature of the solvent, degree of cross-linking, nature of the fixed ionic groups, and the capacity of the resins (9). The polymer swelling facilitates the penetration of the acid into the resin phase. The solvation of the polymeric chain was also found to contribute to the swelling. The resin swelling, by both the acid and solvent, was thus found to be significant (9).

The ability of weakly basic ion-exchange resins to preferentially remove acetic acid from ethyl acetate has been established from equilibrium studies (9). However, the applicability of the adsorption process depends on the mass transfer rate of acid into the resin phase, the ease of resin regeneration, and the recyclability of the resin. Therefore, evaluation of kinetic behavior of the separation process is important. Adsorption at the functional sites is considered to be very fast, but the uptake rate can be slowed down due to interphase and intraparticle mass-transfer resistances. Mass transfer by diffusion occurs in the film near the solid/liquid interface while the intraparticle mass transfer through the swollen resin structure is probably due to pore diffusion or is a combination of facilitated diffusion over a polymer structure, which is a process akin to surface diffusion, and pore diffusion.

Although several review papers have been published on adsorption kinetics from aqueous solutions (12–14), no significant studies have been reported on mass transfer of acetic acid into such polymeric resin phases from nonaqueous solutions. However, a number of researchers have considered mass transfer of solutes in polymeric adsorbents from aqueous solutions and a few from nonaqueous phases (15–17). During adsorption of benzaldehyde from methanol and aqueous solutions, pore diffusion was found to be dominant when adsorption affinity was small, while surface diffusion was dominant when the adsorption affinity was high (15). A similar surface diffusion controlling process was observed during adsorption of phenols from aqueous solutions on Amberlite XAD-4 (16) and adsorption of dichlorophenol and nitrophenol on polymeric adsorbents (17). In these cases, the mass transfer rates were higher than could be explained by pore diffusion alone, and mass transfer in the sorbed phase had to be considered in parallel with pore diffusion.

However, in several other cases, pore diffusion was reported to be dominant to surface diffusion. A few notable references include adsorption of phenols from aqueous solutions on Duolite ES861 (18), adsorption of various amino acids on XAD-4 (19), adsorption of antibiotic cephalosporin C on brominated Amberlite XAD-2 (20), and adsorption of phenylalanine using similar porous polymeric adsorbents (21).

The results from diffusivity studies on different species in similar types of polymeric adsorbents show that intraparticle mass transfer resistance is often dominant. Because no clear criteria exist for a priori determination of the importance of pore diffusion and/or surface diffusion, we decided to determine experimentally the effective diffusivity of acetic acid in the resin phases. Because structure of the functionalized resins differs with manufacturing process and degree of cross-linking, the experimental determination of diffusion rates was necessary. The diffusivity of the acid through the resins is a function of resin swelling because the movement of acetic acid through the resin is facilitated in a swollen resin. The rate of mass transfer will thus be dependent on the extent of resin swelling. Many organic solutes adsorbed from aqueous solutions on polymeric adsorbents are recovered by solvent regeneration, mostly through the use of polar solvents, such as methanol or acetone. Although the regeneration kinetics may become the controlling mechanism in the overall operation, the diffusion behavior of solutes in polar solvents has rarely been reported in the literature.

## MATERIALS AND REAGENTS

S. D. Fine Chemicals (Mumbai, India) supplied acetic acid. Lakshmi Organics Ltd (Mumbai, India) supplied ethyl acetate and ethanol. The weak (Indion 850) and the strong (Indion 810) anion exchange resins were manufactured by Ion Exchange (India) Ltd (Mumbai, India). The other weak anion exchange resin (Tulsion A-8X MP) was manufactured by Thermax Ltd (Pune, India). Both Indion 850 and Tulsion A-8X MP resins have similar structures. The detailed characteristics of the IERs are reported in Table 1.

***Table 1.*** Properties of Ion Exchange Resins

| Properties | Indion 850 | Tulsion A-8X MP | Indion 810 |
|---|---|---|---|
| Type | weak base macroporous | weak base macroporous | strong base macroporous |
| Matrix structure | styrene-divinylbenzene copolymer | styrene-divinylbenzene copolymer | styrene-divinylbenzene copolymer |
| Functional group | $-NR_2$ | $-NR_2$ | $-N^+R_3$ |
| Particle size (m) $\times 10^{-3}$ | 0.3–1.2 | 0.3–1.2 | 0.3–1.2 |
| Ionic form | free base | free base | $OH^-$ |
| Diameter of resin (m) | 0.00075 | 0.00075 | 0.00075 |
| Surface area ($m^2$/kg) | $35 \times 10^3$ | $23 \times 10^3$ | $27.7 \times 10^3$ |
| Pore volume ($m^3$/kg) $\times 10^{-3}$ | 0.5229 | 0.2374 | 0.2596 |
| Pore diameter (nm) | 33.9 | 19.5 | 29.0 |
| Exchange capacity (mol/kg dry resin) | 3.0 | 2.6 | 2.2 |
| Percentage cross-linking (as given by manufacturers) | 7–8 | — | 7–8 |
| Internal voidage of resin | 0.39 | 0.21 | 0.29 |

—Data not available.

## EXPERIMENTAL METHODS

### Conditioning of the Resins

The resins were washed with 5% (wt/vol) solutions of sodium hydroxide, and the excess alkali was removed by a large volume of distilled water. The resins were then washed with methanol, oven dried for 6 hours at 333 K, and subsequently cooled to room temperature (303 K).

### Kinetic Studies

The kinetic studies were conducted in a 3-necked, fully baffled glass, cylindrical vessel (100 mL). A known quantity of resin was placed in the vessel and then a solution of acetic acid in ethyl acetate was added. The suspension was agitated with a 6 flat-blade turbine impeller at 1600 rpm. Kinetic experiments were initially carried out at different stirrer speeds (500, 1000, 1500, and 2000 rpm) to establish the minimum speed required to eliminate external mass-transfer resistance. Above 1500 rpm, the external mass-transfer resistance was determined to be negligible because the concentration profiles did not change with the increase

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in speed of agitation beyond 1500 rpm (2,11). Samples were withdrawn from the suspension at regular intervals for residual acid concentration. After completion of a typical 20-minute experiment, the resin beads were removed from the vessel and examined microscopically for breakage. No breakage of the beads was visible.

For the acid concentration determination, the supernatant solution was separated from the resins and then was washed with water to transfer acetic acid to an aqueous phase, which was then analyzed titrimetrically against a standardized NaOH solution. No appreciable ethyl acetate hydrolysis was detected during the phase transfer and subsequent titrations. The alcohol was of the azeotropic composition (95% alcohol and 5% water) in all experiments unless otherwise stated. For the analysis of acetic acid in alcohol, the supernatant solution was diluted with water and titrated with a standard NaOH solution.

### Column Studies

The feed consisting of acetic acid in ethyl acetate at a known concentration was pumped with a high-pressure duel-reciprocating pump with adjustable flow rates through a glass column packed with Indion 850, a weakly basic ion-exchange resin. The upward flow of liquid was chosen to minimize channeling within the bed as far as possible. For uniform packing of the column, the top and the bottom zones were packed with small glass beads (1 mm in diameter) to minimize dead volume and end effects on mass transfer in the column. Samples were withdrawn from the outlet stream at constant intervals. The adsorption run was continued until the outlet concentration became equal to the inlet concentration. The adsorption runs were followed by desorption runs. The recyclability of the resin was also checked by up to 5 adsorption and desorption cycles.

## RESULTS AND DISCUSSION

The uptake of acetic acid from the organic phase by basic resins can be described in terms of sorption reinforced by specific interactions of the acid with the functional group in the resin phase (9). The adsorption takes place by formation of hydrogen-bonded complexes between the acid and functional group of the IERs. The maximum swelling in pure ethyl acetate was exhibited by Indion 850 resins (19%) and to a lesser extent by Tulsion A-8X MP resins (9%), while Indion 810 resins exhibited a negligible swelling (1%). In aqueous conditions, all 3 resins exhibited negligible swelling. The tendency of the Indion 850 resins to swell more than the Tulsion A-8X MP resins probably accounts for the difference in the acid uptakes by these otherwise similar resins. The swelling of resins makes the ad-

*Table 2.* Langmuir Adsorption Isotherm Parameters

| | Ethyl Acetate | | | Ethanol | | |
|---|---|---|---|---|---|---|
| Resin | $K$ dm$^3$/mol | $\Gamma^{\infty}$ mol/kg | % error | $K$ dm$^3$/mol | $\Gamma^{\infty}$ mol/kg | % error |
| Indion 850 | 3.2 | 12.1 | 4.4 | 2.1 | 9.6 | 3.4 |
| Tulsion A-8X MP | 2.1 | 7.0 | 5.0 | 0.9 | 6.5 | 4.3 |
| Indion 810 | 1.9 | 3.8 | 2.0 | 0.8 | 3.1 | 2.3 |

sorption sites more accessible to solute for the formation of hydrogen-bonded complexes. Therefore, we modeled the kinetic and column studies after considering the overall adsorption process to follow the Langmuir adsorption isotherm in the form

$$\frac{\Gamma}{\Gamma^{\infty}} = \frac{KC}{1 + KC} \tag{1}$$

The fitted values of equilibrium constant and loading capacity are reported in Table 2 and Fig. 2. The same parameters are utilized in the simulation. The adsorption data did not fit well in Freundlich's isotherm.

The differences in the sorption of acid from ethyl acetate and ethanol can be explained in terms of activity coefficients and resin swelling. The difference in solvation of acetic acid in bulk organic phase results in a nonideal solution that

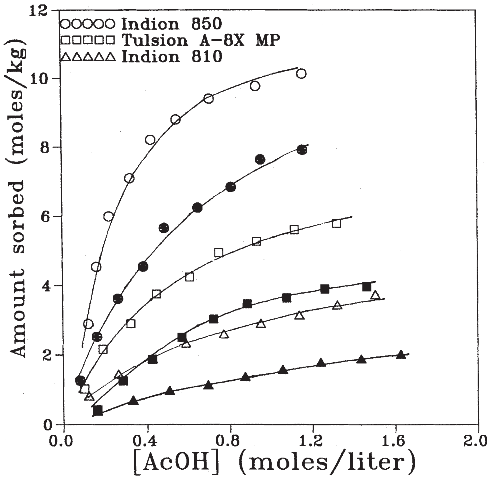


***Figure 2.*** Adsorption of acetic acid from ethyl acetate and azeotropic ethanol on different basic resins at 303 K and fitted in the Langmuir adsorption model (hollow symbols: ethyl acetate; filled symbols: ethanol).

helps or retards the adsorption on the solid surface. The activity coefficient of acetic acid is less than but closer to unity in the alcohol phase and is close to 2 in the ethyl acetate phase. This difference in activity coefficients explains to a large extent the adsorption behavior in these solvents. Although the solvation of the polymer chains and consequent resin swelling were more or less the same; Indion 850 resin swells more than Tulsion A-8X MP resin. This difference in swelling probably accounts for the difference in the acid uptakes by these, otherwise similar, resins. The swelling of resins makes the adsorption sites more accessible to solute. In addition, because of its polar nature and the ability to function both as a hydrogen bond donor and acceptor, ethanol competes with acetic acid, albeit weakly, for sorption in the swollen resin (9).

## Kinetic Studies

Several mechanisms have been proposed to describe internal mass transfer, such as pore diffusion, surface diffusion, or a combination of both mechanisms, and distinguishing between these different transport mechanisms to explain adsorption of resins that undergo swelling because of solvent and solute is difficult. Therefore, the experimentally determined effective diffusivity, which is a combination of all these mechanisms, was evaluated from kinetic studies.

The experimental data were fitted into model Eqs. (2–6) to estimate effective diffusivity of the acid.

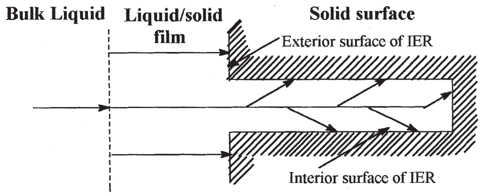
## Model for the Kinetic Studies

We propose a 3-step kinetic model of the adsorption process. The first step consisted of diffusion of the acid through a liquid film surrounding the resin to the resin surface; the second step consisted of diffusion of the acid through the resin to the internal surface area or functional groups; and the third step involved adsorption of the acid on the sites. Figure 3 shows the schematic representation of solute diffusion into the resin phase. A nonlinear concentration profile is expected within the resin phase because adsorption and diffusion are parallel inside the resin phase.

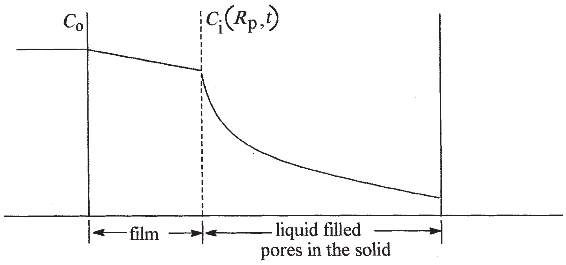
A mass balance in the bulk liquid phase describes the relation between the decreasing acid concentration and mass transfer into the resin phase and can be written as

$$-V_o \frac{dC_o}{dt} = K_s a_{pt}[C_o = C_i(R_p,t)] \tag{2}$$

The mass flow rate of the solute through the external film is proportional to the difference between bulk phase acid concentration ($C_o$) and acid concentration at the particle surface, $C_i(R_p,t)$.



**Sketch of a pore**



**Solute concentration of the liquid phase**

***Figure 3.*** Schematic representation of the solute diffusion into the resin phase.

The mass balance within the particle at a distance $r$ from the center of particle is

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2 D_e \frac{dC_i}{dr}\right] = \varepsilon_i \frac{dC_i}{dt} + \rho_p(1-\varepsilon_i)\frac{d\Gamma}{dt} \tag{3}$$

The second term in the right-hand side of the equation gives accumulation of the acid in the sorbed phase. $D_e$ is effective diffusivity of the acid in the resin phase and should be treated as a combination of pore diffusion and surface diffusion coefficients.

The mass balance equation that depicts the resin phase is based on the assumption that local equilibrium is instantaneous at the active site; that is, no resistance exists in the actual adsorption step.

$$\frac{d\Gamma_i}{dt} = \left(\frac{d\Gamma_i}{dC_i}\right)\left(\frac{dC_i}{dt}\right) \tag{4}$$

The adsorbed phase concentration ($\Gamma$) was approximated using the Langmuir adsorption isotherm (Eq. 1). Although assumptions of the Langmuir model are generally not fulfilled by these adsorbents, this equation provides a useful empirical representation of the adsorption isotherm from equilibrium studies (9).

The initial conditions are

At $t = 0$, $C_i(r,0) = 0$ and $C_o(0) = C_f$

and boundary conditions are

$$D_e \frac{dC_i}{dr} = k_{sl}[C_o - C_i(R_p,t)]; \qquad \text{at } r = R_p \tag{5}$$

$$\frac{dC_i(0,t)}{dr} = 0; \qquad \text{at } r = 0 \tag{6}$$

The external solid-liquid mass transfer coefficient was estimated from an empirical correlation given by Levin and Glastonbury (22) for an agitated slurry.

$$\frac{k_{sl}d_p}{D_m} = 2.0 + 0.47\left(\frac{\varepsilon d_p^4}{\nu_L^3}\right)^{0.21}\left(\frac{d_s}{d_t}\right)^{0.17}\left(\frac{\mu_L}{\rho_L D_m}\right)^{0.36} \tag{7}$$

where $k_{sl}$ is the solid-liquid mass transfer coefficient (m/s); $d_p$ is the diameter of the particle ($0.75 \times 10^{-3}$ m); $D_m$ is the molecular diffusivity of solute (m$^2$/s); $\nu_L$ is the kinematic viscosity of the liquid ($5.543 \times 10^{-7}$ m$^2$/s); $\mu_L$ is the viscosity of the liquid ($0.5 \times 10^{-3}$ kg/m·s for ethyl acetate and $1.5 \times 10^{-3}$ kg/m·s for ethanol); $\rho_L$ is the density of the liquid (902 kg/m$^3$ for ethyl acetate and 785 kg/m$^3$ for ethanol); $d_s$ is the diameter of the impeller ($2 \times 10^{-2}$ m); $d_t$ is the diameter of the vessel ($6 \times 10^{-2}$ m); and $\varepsilon$ is the energy dissipation rate (m$^5$/kg·s$^3$).

The energy dissipation rate per unit weight of the solution was determined using the Eq. (8) (22)

$$\varepsilon = \frac{N_p n^3 d_s^5}{M} \tag{8}$$

where $N_p$ is the power number (5.2 for the 6-bladed turbine); $n$ is the speed of the stirrer (26.67 rps); $d_s$ is the diameter of the turbine ($2 \times 10^{-2}$ m); and $M$ is the mass of the reacting fluid (0.068 kg). The energy dissipation rate was thus estimated to be 0.005 m$^5$/kg·s$^3$.

The liquid molecular diffusion coefficient ($D_m$) was evaluated from the Wilke-Chang correlation (23):

$$D_m = (117.3 \times 10^{-18})T\frac{(\varphi M_B)^{0.5}}{\mu V_A^{0.6}} \tag{9}$$

where $M_B$ is the molecular weight of the solvent (88.1 for ethyl acetate and 46 for ethanol); $T$ is the absolute temperature (303 K); $\mu$is the viscosity of the solution ($0.5 \times 10^{-3}$ for ethyl acetate and $1.5 \times 10^{-3}$ kg/m·s for ethanol); $V_A$ is the solute molal volume at normal boiling point (0.0592 m$^3$/kmol); and $\varphi$ is the association factor for the solvent (1.0 for ethyl acetate and 1.5 for ethanol). The values were taken from *Perry's Chemical Engineer's Handbook* (24).

The molecular diffusivity of acetic acid in ethyl acetate was estimated to be 3.638 $\times 10^{-9}$ m$^2$/s and in ethanol it was $1.4 \times 10^{-9}$ m$^2$/s. The estimated $k_{sl}$ values in ethyl acetate and ethanol were $7 \times 10^{-5}$ and $3 \times 10^{-5}$ m/s, respectively.

Equations (2–4) were solved by the orthogonal collocation method in which the model equations were discretized in $N$ ($N = 10$) collocation points, including

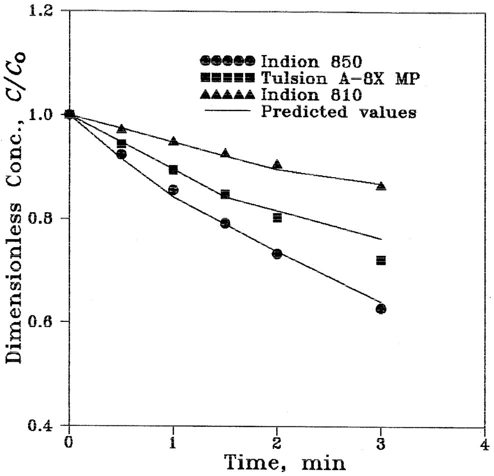


*Figure 4.* Kinetic studies of acetic acid adsorption from ethyl acetate on different resins.

the boundary point $r/R_p = 1$ (25). As a result, the partial differential model equations were transformed into a system of ordinary differential equations that could be solved by the Runge-Kutta fourth-order method. The experimental data were fitted in the model equations to estimate effective diffusivity of acetic acid in the resin phase.

The plots of solute concentration versus time for acetic acid uptake from ethyl acetate by different resins are shown in Fig. 4. The continuous curves denote fitted values from the model while the points represent the experimental values. The effective diffusivity values estimated by fit of the experimental data in the model are reported in Table 3. The polymeric resins as functional adsorbents gave

***Table 3.*** Diffusivity Coefficients, Porosity, and Tortuosity Values

| Resin → | Indion 850 | | Tulsion A-8X MP | Indion 810 |
|---|---|---|---|---|
| Solvent → | Ethyl Acetate | Ethanol | Ethyl Acetate | Ethyl Acetate |
| Effective diffusivity ($m^2/s$) × $10^9$ | 0.177 | 0.09904 | 0.0801 | 0.03175 |
| $\varepsilon_i/\tau$ | 0.049 | 0.071 | 0.022 | 0.009 |
| $\varepsilon_i$ | 0.39 | — | 0.21 | 0.29 |
| $\tau$ | 7.96 | — | 9.55 | 32.22 |
| Surface diffusivity ($m^2/s$) × $10^{12}$ | 3.24 | 3.48 | 3.86 | 3.12 |

—Data not available.

the effective diffusivity of acetic acid in the range of $10^{-11}$–$10^{-10}$ m$^2$/s in nonaqueous conditions. The external mass-transfer coefficient was of the order $10^{-5}$ m/s while the internal mass-transfer coefficient (for a particle size of $0.75 \times 10^{-3}$ m) was of the order $10^{-7}$, which clearly indicates that the intraparticle diffusivity is dominating the mass transfer of acetic acid into the resin phase.

Solutes diffuse much faster into resin phases than they do in molecular sieves, such as zeolite. In the case of zeolites, diffusivity is of the order of $10^{-17}$ m$^2$/s (26). For a resin with an internal porosity close to 0.3–0.4, the estimated tortuosity based on pore diffusion as the controlling mechanism ($\tau = \varepsilon_i D_m / D_e$) is very high (Table 3). The pore size of the resins (20–35 nm) is significantly larger than the kinetic diameter of the acetic acid molecule (0.4 nm). Therefore, acetic acid should diffuse with almost the same ease through different resins under the usual effects of pore tortuosity and voidage. However, the effective diffusivity of acetic acid is different in different resins. The $D_e$ in Indion 850 is higher than that obtained with Tulsion A-8X MP and is the least in Indion 810. The polymer network swells substantially in organic solvents mainly due to London dispersion forces, and if ionic charges are present, the swelling increases due to repulsive electrostatic interactions. Due to the swelling, the penetration of acid into the resin is facilitated. The sites are more easily accessible to acid in a swollen resin than in a nonswollen resin. The swelling of the resins depends on the extent of cross-linking between the resins and divinylbenzene, which is added to prevent the dissolution of polymer, and the degree of cross-linking was not accurately known for these resins. However, the extent of swelling is different for different resins, with the maximum swelling in pure ethyl acetate exhibited by Indion 850. This difference in swelling probably accounts for the difference in the effective diffusivity values shown by these resins.

Figure 5 also shows plots of solute concentration versus time for the uptake of acetic acid from azeotropic ethanol on Indion 850 resin. The extent of swelling is approximately the same for the resins in these solvents; swelling in ethyl acetate being 19% and that in ethanol about 20%, but the effective diffusivity of acetic acid from ethyl acetate is higher than that from alcohol phase. The presence of water in the azeotropic alcohol phase caused 2% ionization of acetic acid in the solution, which is very small at low concentrations of acid and can be neglected (27).

Even though we made no attempt to check the sorption of water over acetic acid and alcohol, the absence of ionized charges on the weakly basic resins makes the sorption of water almost negligible. However, for sorption of acetic acid from absolute alcohol, the uptake of acetic acid must be higher than the sorption from azeotropic alcohol mainly due to 2 factors: first, solvation of acetic acid in absolute alcohol is poor compared to acetic acid solvation in azeotropic alcohol, and second, the competition water provides sites of acetic acid for adsorption. In the case of weakly basic resins, the absence of charges should reduce the sorption of water. No attempt was made to check the sorption of water over alcohol and acetic

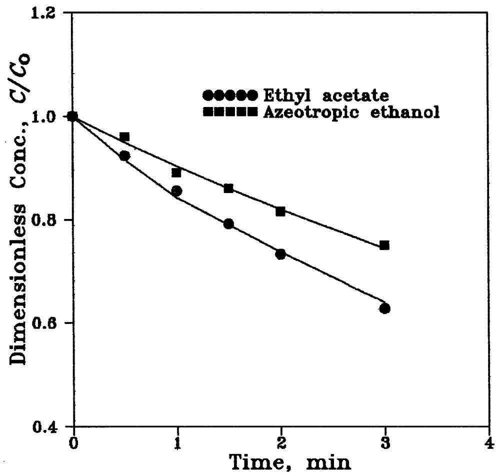


*Figure 5.* Kinetic studies of acetic acid adsorption from ethyl acetate and azeotropic ethanol on Indion 850.

acid and further investigation into this phenomenon may be needed. In all the analysis of experimental data involving azeotropic alcohol, the presence of water was not explicitly considered and all sorption data were generated based on the assumption that the alcohol phase acts as a pseudo-fluid.

The variation in effective diffusivity in different resins and solvents and the very high values of adsorption capacity may point to surface diffusion as the cause of mass transfer. If surface diffusion over the polymer network contributes to mass transfer in the resin phase, then the effective diffusivity is influenced by the adsorbed concentration. The effective diffusivity can be considered a strong function of concentration, but we preferred to treat the diffusion as surface diffusion, which should be dependent on the adsorbed phase concentration. If combined pore and surface diffusions are responsible for mass transfer, then effective diffusivity can be expressed in the form (28)

$$D_e = D_{\text{pore}} + \frac{K\Gamma}{\rho} D_{\text{surface}} \tag{10}$$

For the usual range of pore voidage fraction (0.3–0.4) and a tortuosity factor of 1.5–2.0, the estimated pore diffusivity ($D_e = \varepsilon_i D_m/\tau$) is higher by an order of magnitude than the experimental values. If surface diffusion is considered the primary mechanism of diffusion inside the swollen resin, $D_e$ can be approximated ($D_e \approx K\Gamma\ D_{\text{surface}}/\rho$); i.e., the surface diffusion coefficient $D_{\text{surface}}$ can be estimated from experimental $D_e$. We were surprised to find that the value of $D_{\text{surface}}$ in Indion 850 was almost the same in both solvents. However, the surface diffusion coefficient $D_{\mathrm{surface}}$ for Tulsion A-8X MP is slightly higher but relatively similar to the values in other resins. Although the results do not conclusively support surface diffusion as the primary diffusion mechanism, neither do they support pore diffusion as the only means of diffusion. However, the results point to a significant contribution by surface diffusion. If the surface diffusion is significantly contributing to the overall effective diffusivity, then effective diffusivity is expected to be higher with higher adsorbed phase concentration; the observations are consistent with this deduction.

The experimentally determined effective diffusivity value is very useful for the simulation of the column studies because it also takes into account resin swelling.

## Column Studies

To study the applicability of ion exchange resins for purification of ethyl acetate, column studies were conducted at different flow rates and acid concentrations (Table 4). The dynamic behavior of adsorption columns was also modeled using the equilibrium and kinetic data. The recyclability of the resin was checked by repeated adsorption and desorption cycles on the resin bed under the same conditions as those outlined for run 3 (Table 4).

Figures 6–8 show the adsorption curves for acetic acid from ethyl acetate for different flow rates, concentrations, and dimensions of the column. Run 1 corresponds to the adsorption studies with the feed concentration of acetic acid at 1.8 % (wt/vol). At the breakpoint, when the acid concentration in the exit effluent reached to 5% of feed concentration, the resin bed had adsorbed a total of 0.20 mol

***Table 4.*** Column Adsorption Studies

| Variables | Run 1 | Run 2 | Run 3 | Run 4 |
|---|---|---|---|---|
| Diameter of column (m) | 0.02 | 0.02 | 0.03 | 0.03 |
| Packing height (m) | 0.52 | 0.52 | 0.55 | 0.575 |
| Flow rate ($m^3/s$) $\times 10^7$ | 1.08 | 1.17 | 1.25 | 1.33 |
| Initial concentration ($mol/dm^3$) | 0.31 | 0.22 | 0.50 | 0.11 |
| Mode of flow | Upward | Upward | Upward | Upward |
| Desorbent used | — | ethyl acetate | Azeotropic ethanol | Azeotropic ethanol |
| Desorbent flow direction | — | Downward | Downward | Downward |
| Percentage of solute (wt/vol) | 1.86 | 1.32 | 3.0 | 0.66 |

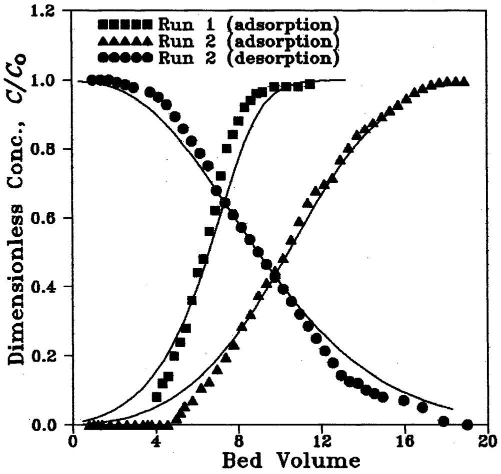


***Figure 6.*** Adsorption and desorption breakthrough curves for acetic acid in ethyl acetate on Indion 850 (run 1 and 2).

of AcOH. This amount corresponds to the loading capacity of 4.7 mol/kg resin, which is slightly higher than that predicted from the subsequently described column model. At the breakpoint, complete bed capacity had not been used, and the experimental efficiency of the resin bed was 72%. On complete saturation of the

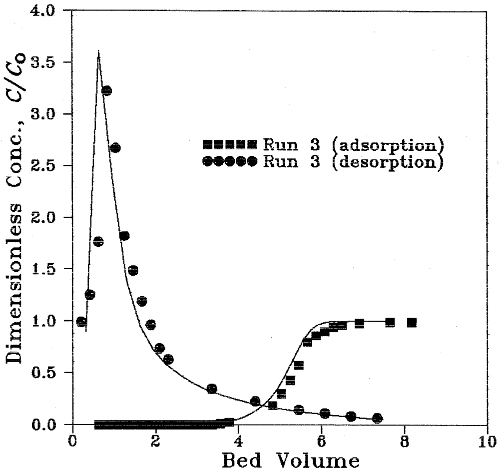


***Figure 7.*** Adsorption and desorption breakthrough curve for acetic acid in ethyl acetate on Indion 850 (run 3).

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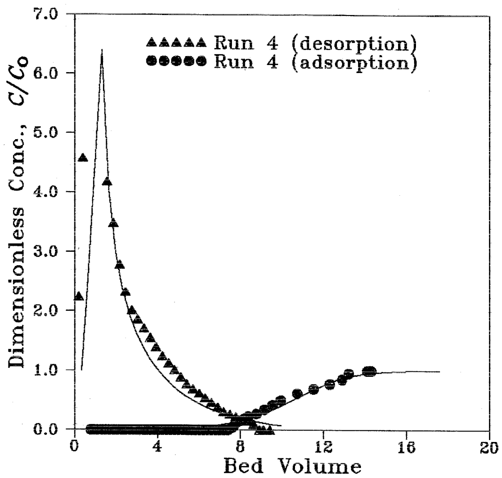

***Figure 8.*** Adsorption and desorption breakthrough curve for acetic acid in ethyl acetate on Indion 850 (run 4).

bed, for which 11.5 bed volumes of the feed solution were required, the bed showed the capacity of 6.8 mol/kg resin. This amount matches well with that expected from the equilibrium studies; i.e., the saturation capacity of the adsorbent bed can be fully utilized.

At a lower feed concentration of the acid at 1.32% (wt/vol) (run 2), the breakpoint occurred at 5.4 bed volumes where the resin bed had adsorbed approximately 0.194 mol of AcOH. The corresponding loading capacity of the resin was 4.1 mol/kg adsorbent. From the equilibrium studies, the loading capacity at the given feed concentration was determined to be 6.1 mol/kg adsorbent. For complete saturation of the bed, 17 bed volumes of the feed solution were required and the bed showed the capacity to adsorb 6.2 mol/kg resin.

Figure 6 also shows the desorption curve of the acid when acid-free ethyl acetate was passed through the saturated column. Approximately 18 bed volumes of ethyl acetate, equal to that required for adsorption, were required for complete regeneration of the resin bed. No significant difference was observed in adsorption and desorption rates.

The acid can be completely desorbed by alkaline solutions of appropriate strength because the affinity of acetate ions for the resin is negligible. Although just 1 bed volume alkali solution of 1.0 % (wt/vol) strength was sufficient to desorb acetic acid from the loaded column, this process may not be practically attractive. The resin must be washed with water to remove the excess alkali after treatment because the presence of alkali can cause hydrolysis of ethyl acetate during the following adsorption run. Drying the resin is necessary to maintain the adsorption capacity of resin, but direct drying of the resin bed after the water wash causes the resin beads to shrink and block the resin pore openings. The resulting bed shrinkage may result in reduced capacity. The water wash should be followed by an alcohol wash to remove water from the resin pores and then the resin should be dried. This extra wash step makes the overall process cumbersome and less attractive.

The regeneration efficiency of styrene-divinylbenzene resins by organic solvents increases with a decreasing solubility parameter of the solvent (29). The most efficient solvents are low molecular-weight alcohols and ketones. If a solvent with a solubility parameter lower than that of ethyl acetate is used, then more efficient desorption of the acid is expected. The adsorption equilibrium studies from azeotropic ethanol showed the reduced tendency of the acid to adsorb (9). Thus alcohol, with a solubility parameter of 12.7, can be used as a desorbent (30).

Figure 7 shows the adsorption studies with a feed acid concentration of 3% (wt/vol) (run 3). The breakpoint occurred at 3.8 bed volumes where the resin bed had adsorbed 0.725 mol of AcOH. The corresponding loading capacity of the resin was 5.7 mol of AcOH/kg resin. For the complete saturation of the bed, 8 bed volumes of the feed solution were required. The capacity of the resin bed at complete saturation was 8.4 mol/kg resin, which matches well with the equilibrium studies. The AcOH desorption from the loaded column was carried out by passing azeotropic alcohol in the reverse direction (Fig. 7). The rate of desorption was initially very fast and resulted in the eluent acid concentration increasing to more than twice the initial feed concentration. The presence of ethanol decreased the interaction between acetic acid and the functional group of the resin, leading to removal of the acid from the sites and thus increasing the concentration of acetic acid in the eluent. Six bed volumes of the alcohol were required to regenerate the bed completely.

Figure 8 gives the adsorption and desorption curves at a still lower concentration of acetic acid in the feed solution (0.66% wt/vol) (run 4). The breakpoint occurred at 7.5 bed volumes where the resin bed could adsorb 0.34 mol of AcOH. The corresponding loading capacity of the resin was 2.0 mol/kg adsorbent. According to the equilibrium studies, the loading capacity at this feed concentration should have been 2.85 mol/kg adsorbent. Fourteen bed volumes of the feed solution were required for complete saturation. The capacity of the resin bed at complete saturation was 2.8 mol/kg adsorbent, which also matched well with the equilibrium studies. The AcOH desorption from the loaded column was carried out by passing azeotropic alcohol through the column (also shown in Fig. 8). Eight bed volumes were required to regenerate the bed.

An additional advantage of using ethyl alcohol for desorption of acid from the loaded column can be gained if the eluted alcohol-acid mixtures are recycled to the esterification reactor because the cost of the purification process can be significantly reduced. However, if the alcohol-acid mixtures cannot be recycled, then the overall economics of the adsorption process, coupled with distillation to separate these mixtures, will be a key factor in the determination of the suitability of the adsorption process.

### Recyclability Studies

The recyclability of the ion exchange resins was checked by using the same resin bed for repeated runs. The column details for the recyclability studies are the same as those given for run 3 (Table 4).

The first adsorption run was stopped at the breakthrough point and the desorption run was started in the reverse direction. The desorption run was stopped when the concentration of acetic acid in the outlet stream reached 2% of the feed concentration. At this point, 88.4% of acetic acid had been removed from the bed. Approximately 2.2 bed volumes were required to bring acetic acid concentration to this value, which is one-half the number of bed volumes treated in the adsorption run. According to material balance calculations, the column still retained approximately 11.6% of the adsorbed acid. The next adsorption run was started again in the forward direction. The breakpoint occurred at 3.3 bed volumes at which the adsorbed acetic acid corresponded to the amount desorbed in the previous regeneration step and remained the same for all subsequent adsorption cycles. The adsorption and desorption cycles were repeated 5 times without affecting the capacity of the resin. No appreciable degradation or loss of capacity was observed for the resin. The capacity of the bed remained at 5.1 mol/kg and could be regenerated and sustained throughout all adsorption-desorption cycles.

### Simulation of Column Studies

A linear driving force model was used to simulate the adsorption-desorption cycles (31). The numerical complexities involved in the solution of the model were overcome by using a lumped parameter model so that the intraparticle concentration, $C_\mathrm{i}(r,t)$, becomes only a function of time; i.e., volume average concentration $C_\mathrm{i}(t)$ is defined as follows:

$$C_\mathrm{i}(t) = \frac{1}{V_\mathrm{p}} \int C_\mathrm{i}(r,t)dV \tag{11}$$

Applying the volume average operator, the modeling equations are as follows:

Mass balance in the external liquid phase

$$\varepsilon_e \frac{dC_\mathrm{o}}{dt} + u \frac{dC_\mathrm{o}}{dz} + D_\mathrm{L}\varepsilon_e \frac{d^2C_\mathrm{o}}{dz^2} = K_\mathrm{L} \frac{3}{R_\mathrm{p}} (1 - \varepsilon_e)(C_\mathrm{o} - C_\mathrm{i}) \tag{12}$$

Mass balance in the internal liquid phase (i.e., within the adsorbent particle)

$$\varepsilon_i \frac{dC_{\mathrm{o}}}{dt} = K_{\mathrm{L}} \frac{3}{R_{\mathrm{p}}} (C_{\mathrm{o}} - C_{\mathrm{i}}) - (1 - \varepsilon_i)\rho_p \frac{d\Gamma}{dt} \tag{13}$$

Mass balance in the adsorbed phase with equilibrium at the local level

$$\frac{d\Gamma}{dt} = \left(\frac{d\Gamma}{C_{\mathrm{i}}}\right)\left(\frac{dC_{\mathrm{i}}}{dt}\right) \tag{14}$$

This set of equations (12–14) was solved by the orthogonal collocation method through the discretization of equations along column height, designated as the z-axis, and the resulting set of ordinary differential equations was solved using the Runge-Kutta fourth-order method.

## Parameters of Model

The overall mass transfer coefficient, $K_{\mathrm{L}}$, was obtained from

$$\frac{1}{K_{\mathrm{L}}} = \frac{1}{k_{\mathrm{sl}}} + \frac{1}{k_{\mathrm{i}}\varepsilon_i} \tag{15}$$

where $k_{\mathrm{sl}}$ and $k_{\mathrm{i}}$ are local mass transfer coefficients in the external and internal liquid phases, respectively. The external mass transfer coefficient ($k_{\mathrm{sl}}$) was estimated from the empirical correlation valid for a low Reynolds number ($\mathrm{Re} < 50$) in a packed bed (31)

$$\frac{\mathrm{Sh}}{\mathrm{Sc}^{1/3}\mathrm{Re}} = 0.91\mathrm{Re}^{-0.51}\varepsilon_{\mathrm{l}} \tag{16}$$

where,

$$\mathrm{Sh} = \frac{k_{\mathrm{sl}} d_{\mathrm{p}}}{D_{\mathrm{m}}} \tag{17}$$

$$\mathrm{Re} = \frac{u d_{\mathrm{p}} \rho_{\mathrm{L}}}{6\mu(1 - \varepsilon_e)\varepsilon_{\mathrm{l}}} \tag{18}$$

and

$$\mathrm{Sc} = \frac{\mu}{\rho_{\mathrm{L}} D_{\mathrm{m}}} \tag{19}$$

The estimated external mass transfer coefficient ($k_{\mathrm{sl}}$) was $2.083 \times 10^{-5}$ m/s.

The internal mass transfer coefficient ($k_{\mathrm{i}}$) was estimated using a correlation based on the effective molecular diffusivity ($D_{\mathrm{e}}$) in the particle and the tortuosity factor (given in Table 3) (32).

$$k_{\mathrm{i}} = 5\,\frac{D_{\mathrm{e}}}{R_{\mathrm{p}}\tau} \tag{20}$$

The external mass transfer coefficient was of the order of $10^{-5}$ while the internal mass transfer coefficient was of the order of $10^{-7}$, which clearly indicates that the intraparticle diffusivity is controlling the mass transfer of the acid into the resin phase. The overall mass transfer coefficient ($K_{\mathrm{L}}$) was $1.142 \times 10^{-7}$ m/s in ethyl acetate.

The dispersion coefficient ($D_{\mathrm{L}}$) can be estimated using the empirical correlation that is valid for liquid flow in packed beds (33).

$$\varepsilon_e \mathrm{P_e} = 0.2 + 0.011\,\mathrm{Re}^{0.48} \tag{21}$$

where,

$$\mathrm{P_e} = \frac{u d_{\mathrm{p}}}{\varepsilon_e D_{\mathrm{L}}} \tag{22}$$

$$\mathrm{Re} = \frac{u d_{\mathrm{p}} \rho_{\mathrm{L}}}{\varepsilon_e \mu_{\mathrm{L}}} \tag{23}$$

The loading capacities and equilibrium constants were obtained from the single component batch studies (Table 2). Figures 6–8 also show the predicted curves from the model equations; they match well with the experimental data points for the adsorption and desorption runs. Therefore, dynamic behavior of the adsorption column can be successfully predicted.

The successful simulation of the column behavior from the equilibrium studies indicates a possibility of simulating the combined system of the adsorption column with a distillation column that can be used for bulk separation of acetic acid and ethyl acetate mixtures. The distillation column can be operated at a lower reflux to allow a certain amount of acid in the distillate. The final removal of the acid can be accomplished by the adsorption in ion exchange resin columns. The eluent from the adsorption column after desorption, such as acid and alcohol mixtures, can be recycled to the esterification reactor to reduce the overall cost of the operation. The combination of adsorption with distillation can give a much better purity of ethyl acetate because it will be completely free from the acidic impurities.

## CONCLUSIONS

The removal of acetic acid impurities from ethyl acetate was attempted using commercially available basic ion-exchange resins. The kinetic studies acetic acid adsorption from ethyl acetate and azeotropic ethanol on different basic ion-exchange resins show that the transfer of the acid into the resin phase is controlled by intraparticle diffusion with surface diffusion probably the main contributor to the mass transfer. Results from column studies established that the removal of acetic acid impurities can be successfully carried out by adsorption on ion exchange resins because desorption was effectively carried out with azeotropic ethanol. According to recyclability studies, no appreciable degradation or loss of capacity was observed for the resin even after repeated adsorption-desorption cycles. The dynamic behavior of adsorption columns was also modeled successfully using the equilibrium and kinetic data. It may be possible to integrate such an adsorption process with a distillation column to separate acetic acid–ethyl acetate mixtures in which the reflux ratio can be substantially reduced.

## NOMENCLATURE

| | |
|---|---|
| $a_{\mathrm{tp}}$ | total area of the particles ($\mathrm{m}^2$) |
| $C$ | equilibrium concentration (mol/L) |
| $C_{\mathrm{o}}$ | concentration of the acid in external liquid phase ($\mathrm{mol/m}^3$) |
| $C_{\mathrm{f}}$ | concentration of acetic acid in the feed ($\mathrm{mol/m}^3$) |
| $C_{\mathrm{i}}$ | concentration of acid in internal liquid phase ($\mathrm{mol/m}^3$) |
| $D_{\mathrm{e}}$ | effective diffusivity ($\mathrm{m}^2$/s) |
| $D_{\mathrm{L}}$ | dispersion coefficient ($\mathrm{m}^2$/s) |
| $D_{\mathrm{m}}$ | molecular diffusivity ($\mathrm{m}^2$/s) |
| $D_{\mathrm{pore}}$ | pore diffusivity |
| $D_{\mathrm{surface}}$ | surface diffusivity ($\mathrm{m}^2$/s) |
| $d_{\mathrm{p}}$ | diameter of particle (m) |
| $d_s$ | diameter of the impeller (m) |
| $d_{\mathrm{t}}$ | diameter of the tank (m) |
| $K$ | equilibrium constant from Langmuir equation (L/mol) |
| $k_{\mathrm{sl}}$ | external solid-liquid mass transfer coefficient (m/s) |
| $K_{\mathrm{L}}$ | overall mass-transfer coefficient (m/s) |
| $k_{\mathrm{i}}$ | internal mass-transfer coefficient (m/s) |
| $M$ | mass of liquid, kg |
| $M_{\mathrm{B}}$ | molecular weight of the solvent |
| $N$ | speed of agitation, rps |
| $N_{\mathrm{p}}$ | power number |
| Pe | Peclet number |
| $r$ | distance from particle center within particle, m |
| Re | Reynolds number |
| $R_{\mathrm{p}}$ | radius of the particle (m) |
| Sc | Schmidt number |
| Sh | Sherwood number |
| $T$ | temperature (K) |

| | |
|---|---|
| $t$ | time (seconds) |
| $u$ | superficial velocity (m/s) |
| $V_o$ | volume of external phase ($m^3$) |
| $V_p$ | volume of packed bed ($m^3$) |
| $V_A$ | solute molal volume at normal boiling point |

## Greek Letters

| | |
|---|---|
| $\varepsilon$ | energy dissipation rate ($m^5/kg\cdot s^3$) |
| $\varepsilon_i$ | pore voidage |
| $\varepsilon_e$ | bed voidage |
| $\rho_p$ | solid density ($kg/m^3$) |
| $\tau$ | tortuosity factor |
| $\Gamma$ | adsorbed concentration (mol/kg dry resin) |
| $\Gamma^\infty$ | maximum adsorbed concentration (mol/kg dry resin) |
| $\nu_L$ | kinematic viscosity of liquid ($m^2/s$) |
| $\mu_L$ | viscosity of liquid ($kg/m\cdot s$) |
| $\rho_L$ | density of liquid ($kg/m^3$) |
| $\varphi$ | association factor |

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