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Valeric Acid Extraction with Tri-*N*-butyl Phosphate Impregnated in a Macroporous Resin. I. Equilibrium and Mass Transfer Rates

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ABSTRACT

Equilibrium and mass transfer data for the extraction of valeric acid from aqueous solutions containing less than 2.5 wt% of acid with a macroporous fresh resin, Amberlite XAD-4, and containing tri-*N*-butyl phosphate (TBP) at 25°C are reported. An equilibrium model, which takes into account the valeric acid physical adsorption by the resin (Freundlich isotherm) and the reactive extraction with the TBP inside the pores, provided a good correlation of experimental data. Valeric acid extraction rates were comparatively faster under the initial conditions of higher TBP concentration in the resin and lower concentration of acid in

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the aqueous phase. Intraparticle effective diffusivities were determined using a homogeneous mass-transfer model. A heterogeneous diffusion model which considers parallel diffusion of the TBP–valeric acid complex in the organic phase inside the particle pores and surface diffusion of the valeric acid in the polymeric structure of the resin was employed to derive the pore diffusivity and solid surface diffusivity. Both diffusivities were of the same order of magnitude (10^{-11} m^2/s) showing that both diffusion paths in parallel make significant contributions to the intraparticle mass transfer of valeric acid in the extractant-impregnated resins (EIR).

Key Words: Valeric acid; Extractant-impregnated resin; Particle diffusion kinetics; Adsorption.

INTRODUCTION

Reactive extraction processes have been extensively used for the recovery of carboxylic acids from aqueous solutions. Because of the acid-extractant complexes formed, some advantages of reactive extraction over physical extraction are: higher partition coefficients and selectivities, the organic acids can be stripped with small amounts of water by adjusting the pH of the solution, and smaller equipment for high throughputs can be used.

Organic acids are often found in waste streams of the chemical industry or may be produced as subproducts of chemical reactions. Valeric acid (*n*-pentanoic acid) is a subproduct in the manufacture of adipic acid, used as monomer in polymerization processes, and it must be removed during the adipic acid purification step.

Organophosphorous compounds, such as tri-*N*-butyl phosphate (TBP), have been extensively used as extractants for the recovery of organic acids from aqueous solutions, including fermentation broths and wastewaters. The extraction equilibrium of valeric acid in aqueous solutions with TBP dissolved in kerosene at 25°C has already been reported.[1] Organic membrane contactors have also been used for the extractive ultrafiltration of valeric acid[2–4] and ceramic membranes with TBP-kerosene as solvent.[5]

The use of extractant-impregnated resins (EIR), in which the extractant is immobilized on a solid support by physical interactions,[6–8] is an alternative extraction process that includes the advantages of solid adsorbents for the treatment of dilute solutions. Furthermore, the EIR technique allows the use of fixed or fluidized beds contactors, avoiding the difficulties often encountered when dealing with emulsions. This technique of employing organophosphorous extractants has been used for the recovery of metals,[8–16] tertiary amines for the recovery of citric acid[17–20] and tartaric acid,[20] and trialkylmethylammonium chloride for the extraction of α-phenylglycine.[21,22]

The objective of this work was to determine valeric acid extraction data (equilibrium and mass transfer rates) with a macroporous resin, Amberlite XAD-4, fresh and impregnated with TBP at 25°C. An equilibrium model, which takes into account the physical sorption by the resin and reactive extraction by TBP, provided a good correlation of experimental data. The mechanism of the mass-transfer process has been interpreted using a homogeneous diffusion kinetic model to estimate the intraparticle effective diffusivities of valeric acid and a heterogeneous diffusion model to derive the pore and the solid surface diffusivities.

EXPERIMENTAL SECTION

Reagents

The chemicals used were commercially available and used without further purification: valeric acid (Aldrich, Germany); TBP (tri-*N*-butyl phosphate) (Fluka, Germany); *n*-hexane, acetone, and other chemicals (Panreac, Spain) as analytical reagent grade. Deionized water from a Millipore Milli-Q water system was used throughout the work. The macroporous resin Amberlite XAD-4 (20 to 50 mesh), supplied by Merck, is a styrene–divinylbenzene copolymer with a highly aromatic structure. It has a specific surface area of 75 to 78 $\mathrm{dm^2/kg}$, a porosity of 0.51, an average pore diameter of 5×10^{-8} dm, a particle density of 0.529 $\mathrm{kg/dm^3}$, and an average particle diameter of 7.78×10^{-3} dm. It was washed with acetone and *n*-hexane successively and vacuum-dried at 50°C for 4 hours before impregnation with the extractant.

Impregnation Procedure

Solutions of TBP dissolved in *n*-hexane were employed as impregnating solutions. The impregnation procedure of Amberlite XAD-4 can be found elsewhere.[21]

Equilibrium Experiments

To determine solid–liquid equilibrium data, 0.5 g of either fresh resin or EIR were placed in 0.1 $\mathrm{dm^3}$ Erlenmeyer flasks with 0.05 $\mathrm{dm^3}$ of an aqueous solution of valeric acid of different initial concentrations and no pH adjustment. The sealed Erlenmeyer flasks were placed in a thermostated shaking device at 150 rpm and 25°C for 8 hours. Preliminary experiments showed that equilibrium had been attained after 4 hours. Initial conditions for the equilibrium experiments are shown in Table 1.

The concentration of valeric acid in the aqueous phase was determined by triplicate titrations with standard sodium hydroxide solutions (0.01 to 0.1 M) using phenolphthalein as indicator. The composition in $\mathrm{mol/dm^3}$ was determined with a precision greater than ± 0.001. The pH of the aqueous solution was measured with a Crison pH-meter (accuracy ± 0.01). Valeric acid concentrations in the resin were calculated by a mass balance.

Mass Transfer Rates

Mass transfer rates were determined using a batch-stirred glass tank provided with a turbine-type impeller with a speed controller (ALC quit-S, Conelec HD-250 model). A constant stirring rate of 225 rpm maintained a homogeneous dispersion of 5 g of the resin (fresh or EIR) in $0.5\,\mathrm{dm^3}$ of aqueous phase containing valeric acid at its natural pH. At this stirring speed, the loss of TBP from EIR was negligible. Initial conditions for the mass transfer experiments are shown in Table 2. Temperature and TBP concentration in the EIR were identical to the equilibrium experiments. Once the resin had been added, the timing was started. Aqueous samples of $4\,\mathrm{cm^3}$ were withdrawn at preset time intervals until the equilibrium conditions were reached. Valeric acid concentration and pH were analyzed by the aforementioned methods. Valeric acid concentrations in the resin were determined by a mass balance.

Table 1. Initial conditions of the equilibrium experiments and fitting parameters by Eq. (1) (system *A*) and Eq. (6) (systems *B*, *C*, and *D*).

Experiment	$\bar{C}_{\mathrm{TBPi}}$ ($\mathrm{mol/dm^3}$ fresh resin)	k ($\mathrm{mol^{1\text{-}n}\,dm^{3n}/dm^3}$ fresh resin)	n	K_c ($\mathrm{dm^3/mol}$)
A	0.000	4.955 ± 0.113	0.491 ± 0.006	—
B	0.588	9.161 ± 1.849	0.988 ± 0.032	24.508 ± 0.727
C	1.468	69.569 ± 13.469	1.778 ± 0.066	24.508 ± 0.534
D	2.288	55.171 ± 6.377	1.772 ± 0.057	24.508 ± 0.080

Table 2. Initial conditions and results of the kinetic experiments.

Experiment	C_{Ai} (mol/dm^3)	pH$_i$	x	$\bar{C}_{TBPi}$ (mol/dm^3 fresh resin)	K [Eq. (9)] (dm^3/dm^3 fresh resin)	D_e [Eq. (10)] (m^2/s)
a	0.015	3.32	0.78	1.468	35.737	2.19×10^{-11}
b	0.029	3.25	0.78	1.468	29.525	2.02×10^{-11}
c	0.060	2.88	0.78	1.468	24.088	1.83×10^{-11}
d	0.029	3.25	0.00	0.000	40.005	1.19×10^{-11}
e	0.029	3.25	0.31	0.588	23.060	1.59×10^{-11}
f	0.029	3.25	1.00	2.288	37.033	2.14×10^{-11}

RESULTS AND DISCUSSION

TBP–Amberlite XAD-4 Impregnation

Experimental results showed that TBP concentration impregnated in the EIR lineal increases with the TBP concentration in the *n*-hexane impregnating solution till saturation was achieved for a solution 57 wt% of TBP (not shown). Beyond this concentration, the EIR becomes sticky. Saturation concentration in the EIR was 2.127 mol TBP/kg EIR (or 2.592 mol TBP/dm^3 of fresh resin). The amount of TBP transferred from the n-hexane solutions to the resin was always higher than 98%.

Sorption/Extraction Equilibrium

Figure 1 shows the sorption/extraction equilibrium data of valeric acid with fresh resin and with EIR. The concentration of valeric acid in the resin is higher with fresh resin (system *A*) than with EIR, except for system *D*, which has the highest load of TBP in the EIR. As it might be expected, as the TBP concentration in the EIR increases, the amount of valeric acid extracted also increases. Saturation concentrations of valeric acid in the EIR are also shown in Fig. 1.

The physical adsorption Freundlich model was used for the correlation of the valeric acid adsorption equilibrium data with fresh resin (system *A*):

$$\bar{q} = kC_{HA}^{n} \tag{1}$$

where $\bar{q}$ is the concentration of valeric acid adsorbed in the resin expressed in mol/dm^3 of fresh resin, k and n are the parameters of the Freundlich equation, and C_{HA} is the equilibrium concentration of the undissociated acid in the aqueous phase, in mol/dm^3.

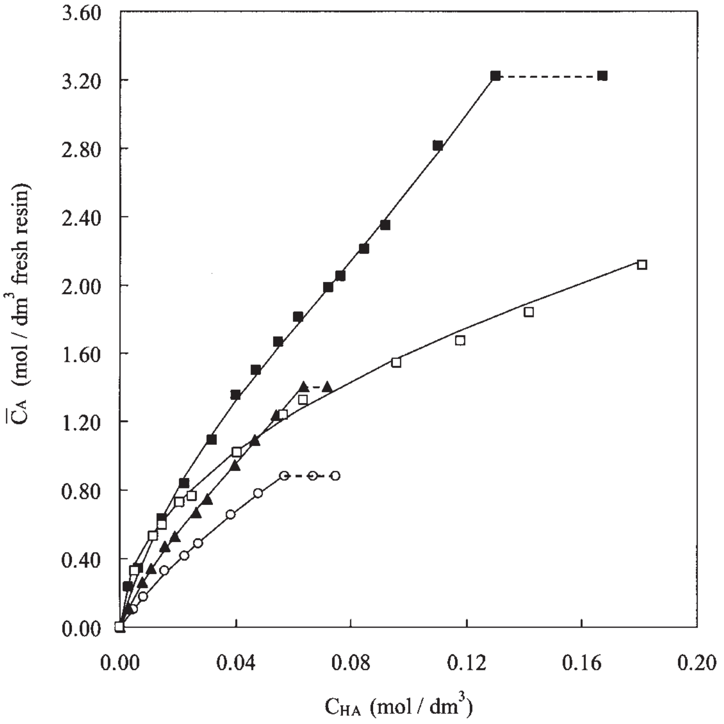

Figure 1. Equilibrium isotherms of valeric acid with fresh resin and with EIR at 25°C under the initial conditions shown in Table 1: (□), experiment *A*; (○), experiment *B*; (▲), experiment *C*; (■), experiment *D*. Solid lines are estimated by Eqs. (1) or (6).

The concentration of undissociated valeric acid in the aqueous phase was calculated by taking into account the partial dissociation of the valeric acid in aqueous phase ($pK_a = 4.86$), the analytical acid concentration in the aqueous phase, C_A, and the pH values, given as:

$$C_{HA} = \frac{C_A}{1 + 10^{pH - pK_a}} \qquad (2)$$

Values of *k* and *n* parameters for Eq. (1), determined using the Levenberg–Marquardt algorithm, and standard deviations of parameters are shown in Table 1.

For systems with EIR, it was assumed that the uptake of valeric acid by EIR takes place by both processes, i.e., adsorption by the resin and reactive extraction with TBP inside the resin pores. The reactive extraction of the valeric acid with TBP yields a TBP–acid complex and can be described by the following reaction equilibrium:[1,5]

$$\mathrm{HA} + \overline{\mathrm{TBP}} \longleftrightarrow \overline{\mathrm{TBPHA}} \tag{3}$$

where the overbars refer to the organic phase. The equilibrium constant for Eq. (3) is given by:

$$K_{\mathrm{c}} = \frac{\bar{C}_{\mathrm{TBPHA}}}{\bar{C}_{\mathrm{TBP}} C_{\mathrm{HA}}} \tag{4}$$

Assuming that the $\overline{\mathrm{TBPHA}}$ species is the only one extracted by the TBP immobilized inside the particle pores, that there is no aggregation in the organic phase inside the pores, and that the solubility of TBP in aqueous solution is negligibly small, the TBP–acid complex concentration can be expressed as:

$$\bar{C}_{\mathrm{TBPHA}} = K_{\mathrm{c}} \frac{\bar{C}_{\mathrm{TBPi}} C_{\mathrm{HA}}}{1 + K_{\mathrm{c}} C_{\mathrm{HA}}} \tag{5}$$

where $\bar{C}_{\mathrm{TBPi}}$ is the initial extractant concentration in the EIR.

The total concentration of valeric acid in the EIR, $\bar{C}_{\mathrm{A}}$, may be expressed as the contribution of two terms: one accounts for the adsorption on the resin, Eq. (1), and the other for the TBP–acid complex extraction, Eq. (5):

$$\bar{C}_{\mathrm{A}} = \bar{q} + \bar{C}_{\mathrm{TBPHA}} = kC_{\mathrm{HA}}^{\mathrm{n}} + K_{c} \frac{\bar{C}_{\mathrm{TBPi}} C_{\mathrm{HA}}}{1 + K_{\mathrm{c}} C_{\mathrm{HA}}} \tag{6}$$

where $\bar{C}_{\mathrm{A}}$, expressed in $\mathrm{mol/dm^3}$ of fresh resin, is obtained by the following mass balance:

$$\bar{C}_{\mathrm{A}} = \frac{V}{\bar{V}} (C_{\mathrm{Ai}} - C_{\mathrm{A}}) \tag{7}$$

V and $\bar{V}$ are the volumes of the aqueous solution and the fresh resin, in $\mathrm{dm^3}$, respectively. The fresh resin volume was estimated from the EIR weight utilized in each experiment, the weight ratio between the EIR and the fresh resin, and the fresh particle density ($0.529\,\mathrm{kg/dm^3}$).

Parameters k, n, and K_{c} of the equilibrium equation, Eq. (6), determined using the Levenberg–Marquardt algorithm, and standard deviations of parameters are shown in Table 1. Different values of k and n were obtained for each impregnation though K_{c} was a constant, independent of the TBP concentration. Its value agrees with the K_{c} value obtained for the solvent extraction of valeric acid with TBP using kerosene as diluent.[1,5] Figure 1 shows the experimental data of equilibrium isotherms (data points) and data fitting to Eqs. (1) or (6) (solid curves), the average standard deviations being lower than 2.5%.

The contribution of extraction and adsorption separately on the valeric acid uptake by the EIR was calculated from Eq. (6) and is shown in Fig. 2. The

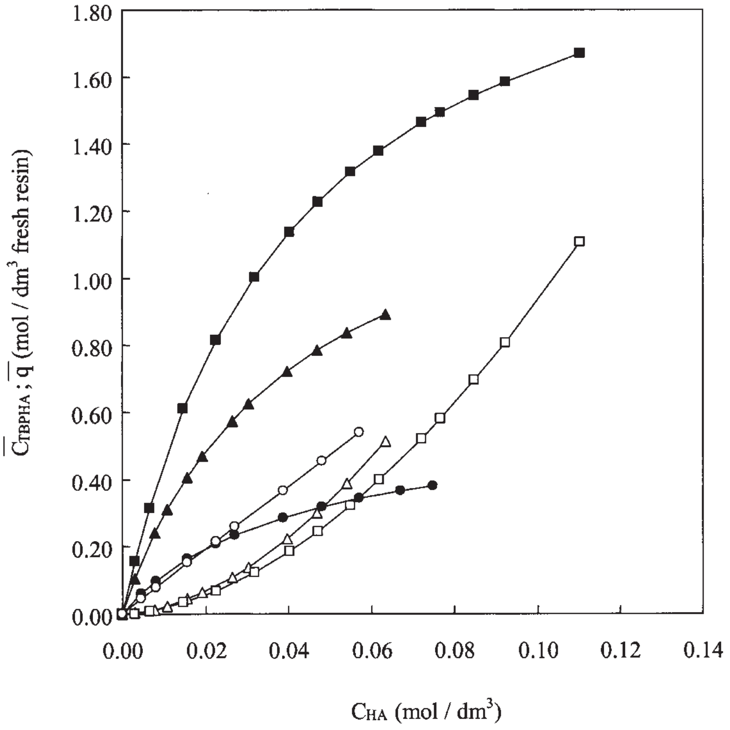

Figure 2. Comparison between the equilibrium valeric acid concentration inside the EIR adsorbed by the resin, $\bar{q}$, and extracted by the TBP inside the particle, $\bar{C}_{\mathrm{TBPHA}}$, for systems shown in Table 1: (○), adsorption in experiment *B*; (●), reactive extraction in experiment *B*; (△) adsorption in experiment *C*; (▲), reactive extraction in experiment *C*; (□), adsorption in experiment *D*; (■), reactive extraction in experiment *D*.

effect of the extraction increases as the load of TBP in the EIR increases, extraction being the main contribution in systems *C* and *D*, however, the contribution of the adsorption is big enough, even when the total volume of the pores is totally filled with TBP (experiment *D*).

Mass Transfer Rates

Concentrations of undissociated valeric acid in the aqueous phase at any time, $C_{\mathrm{HA}}(t)$, were calculated from Eq. (2). The concentration of valeric acid in the resin phase as a function of time, $\bar{C}_{\mathrm{A}}(t)$, was obtained from a mass balance, which takes into account the mass withdrawn with each sample and the volume corrections:

$$\bar{C}_A(t) = \frac{C_{A1}V - C_A(t)\{V - \sum_1^{S-1} V_S\} - \sum_1^{S-1} C_{AS}V_S}{\bar{V}} \tag{8}$$

where $\bar{C}_A(t)$ is expressed in mol/dm^3 of fresh resin; C_{A1} and $C_A(t)$ are the initial and analytical acid concentration in the aqueous phase in mol/dm^3 as a function of time; V is the volume of the initial aqueous phase and $\bar{V}$ is the volume of the fresh resin; and V_S and C_{AS} are the volume and concentration of the aqueous samples withdrawn.

Figure 3 shows the evolution of valeric acid concentration in the aqueous phase with time for the kinetic experiments shown in Table 2. The equilibrium conditions were reached after about 50 to 90 minutes.

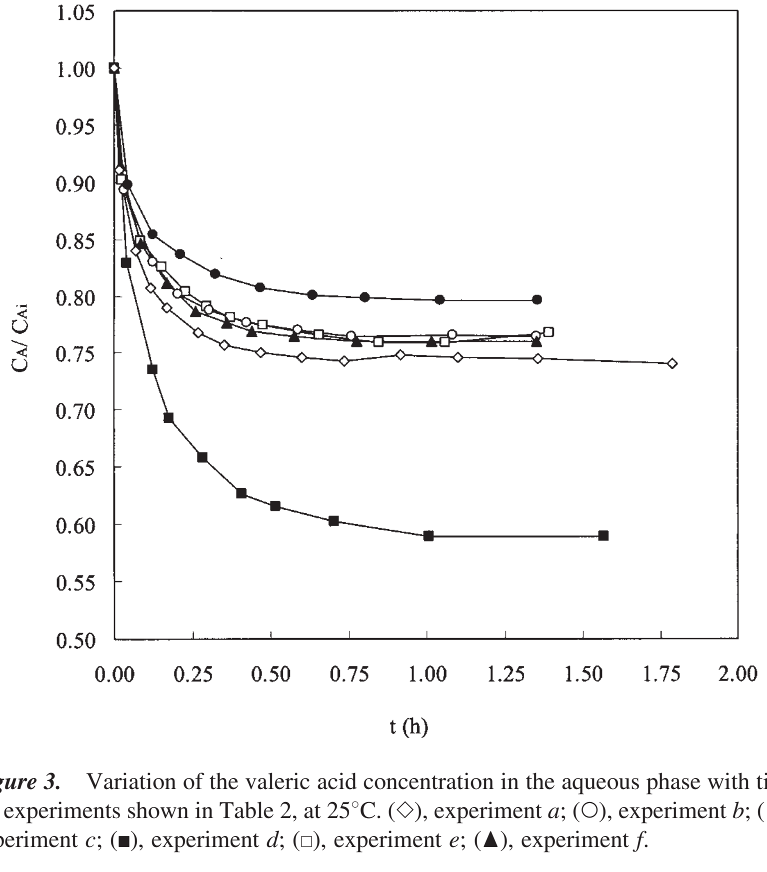

Figure 3. Variation of the valeric acid concentration in the aqueous phase with time for experiments shown in Table 2, at 25°C. (◇), experiment *a*; (○), experiment *b*; (●), experiment *c*; (■), experiment *d*; (□), experiment *e*; (▲), experiment *f*.

Comparison of experiments for the same valeric acid concentration (experiments *b* and *d*–*f*) shows that the rate of acid uptake by the resin increases as the TBP load in the EIR increases, the process with fresh resin (experiment *d*) being the slowest one. These results lead to the conclusion that the chemical reaction rate is fast and it is not the limiting step of the mass-transfer process.

The intraparticle diffusion is usually the rate limiting step in adsorption processes with macroporous adsorbents in well-stirred tanks. A simple homogeneous model based on Fick's second law was used to estimate the effective intraparticle diffusivity in the separation of metals with EIR[11–13,16] and with porous adsorbents.[23,24] It also was applied to the α-phenylglycine extraction kinetic data with Tomac-EIR.[22] Several heterogeneous models have been used to study the contribution of both pore and solid surface diffusion to the total diffusional mass transfer in separation processes with porous materials.[23–29]

In this work, the intraparticle effective diffusivities of the valeric acid uptake were determined from a homogeneous diffusion model. Then, these values were used to calculate the pore diffusivity and the surface diffusivity, assuming parallel paths. Pore diffusion accounts for the transport of the complex TBP–acid inside the extractant-filled macropore and surface diffusion for the transport of adsorbed acid over the particle surface.

Homogeneous Diffusion Model

The homogeneous model based on Fick's second law considers the sorption process of the homogeneous spherical particles of EIR immersed in a stirred aqueous solution of finite volume. The film diffusion resistance to mass transfer is negligible. At the liquid–solid interface, an instantaneous equilibrium is attained and the equilibrium distribution ratio of the species transferred between the EIR and the aqueous solution is *K*, given by Eq. (9). Once the species reach the surface of the EIR, they diffuse slowly into the particle. It is assumed that the acid concentration in the bulk solution varies with time and that the effective diffusivity into the particle is constant.

$$K = \frac{\bar{C}_{\mathrm{A}}}{C_{\mathrm{HA}}} \tag{9}$$

Under these conditions, the fractional amount of solute in a spherical particle after time *t*, with respect to the corresponding quantity at infinite time is given by:[22,30]

$$\frac{M(t)}{M(\infty)} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(1+\alpha)\exp\left(-g_n^2(D_e t/a^2)\right)}{9 + 9\alpha + \alpha^2 g_n^2} \tag{10}$$

where D_e is the intraparticle diffusion coefficient and g_n are the non-zero roots of the following equation:

$$\frac{g_n}{\tan g_n} = 1 + \frac{\alpha g_n^2}{3} \tag{11}$$

where α is the effective volume ratio given as:

$$\alpha = \frac{V}{\bar{V}K} \tag{12}$$

$M(t)$ can be obtained from the total amount of acid transferred from the bulk solution by a mass balance [Eq. (8)], and $M(\infty)$ may be expressed in terms of the parameter α as:

$$\frac{M(\infty)}{VC_{\mathrm{AH_i}}} = \frac{1}{1+\alpha} \tag{13}$$

Identical values of K [Eq. (9)] were obtained by using the mass balance, Eq. (8) at the equilibrium time, or by the equilibrium model, Eqs. (1) or (6). The effective intraparticle diffusivity, D_e, was determined as the best fit of Eq. (10) to the experimental data by minimizing the sum of the square of the differences between experimental results and the calculated data. Values of D_e and K are shown in Table 2. Figure 4 shows the $\log[1 - (M(t)/M(\infty))]$ values as a function of time, t. A close agreement between the measured (data points) and the calculated rates (solid curves) is observed. Average standard deviations below 2% were obtained.

From data shown in Table 2, it is observed that D_e increases and, consequently, the sorption process is comparatively faster under the initial conditions of lower acid concentration in the aqueous phase and higher TBP concentration in the EIR. The equilibrium distribution coefficient, K, also increases under the aforementioned initial conditions, as is shown in Table 2 (systems *a–c*, *e*, and *f*). The equilibrium distribution ratio has an important effect on the rate of the sorption process. As K increases, α decreases and the term $[1 - (M(t)/M(\infty))]$ decreases faster, yielding a comparatively fast sorption process.

Heterogeneous Parallel Diffusion Model

For a polymeric and nonionic macropore adsorbent such as Amberlite XAD, diffusion in both the fluid inside the pores and in the adsorbed phases takes place. In a parallel heterogeneous diffusion both surface diffusion and the macropore diffusion take place simultaneously in parallel and both

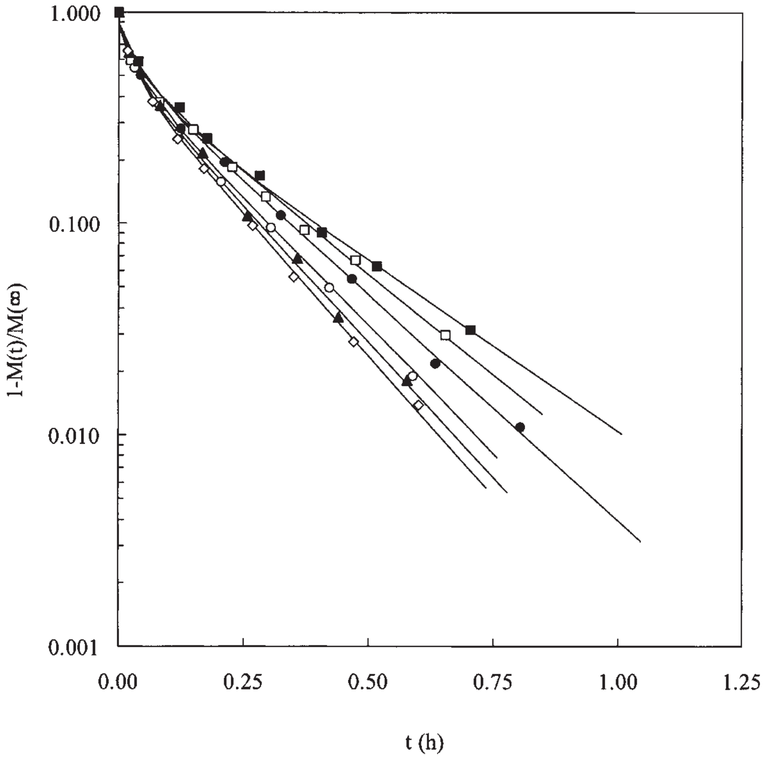

Figure 4. Mass transfer rates of valeric acid, at 25°C, for the experiments shown in Table 2: (◇), experiment *a*; (○), experiment *b*; (●), experiment *c*; (■), experiment *d*; (□), experiment *e*; (▲), experiment *f*. The solid curves were calculated by Eq. (10).

contribute to the total diffusional flux of the adsorbate inside the particle. Assuming that: (1) adsorbent particles are spherical and of uniform size, density, and porosity; (2) there is no convection inside the particles; (3) there is a local equilibrium between the solid phase and the liquid phase inside the particle; and (4) the pore and solid surface diffusivities are constant, the amount of valeric acid inside the resin particles without TBP is given by the following equation:[24–29]

$$\frac{\partial \bar{q}}{\partial t} + \frac{\partial \bar{C}_\mathrm{p}}{\partial t} = D_\mathrm{s}\left(\frac{\partial^2 \bar{q}}{\partial r^2} + \frac{2}{r}\frac{\partial \bar{q}}{\partial r}\right) + D_\mathrm{p1}\left(\frac{\partial^2 \bar{C}_\mathrm{p}}{\partial r^2} + \frac{2}{r}\frac{\partial \bar{C}_\mathrm{p}}{\partial r}\right) \tag{14}$$

where $\bar{C}_\mathrm{p}$ is the undissociated valeric acid concentration in the aqueous phase inside the pores, $\bar{q}$ is the valeric acid concentration adsorbed in the solid phase, both expressed in $\mathrm{mol/dm^3}$ of fresh resin, and D_{p1} and D_{s} are the pore and the solid surface diffusivities, respectively. For the EIR systems, if the assumption is made that TBP fills a fraction of the resin pores volume,[8,22,31] based on Eq. (14), an intraparticle parallel diffusion model can be represented by the following equation:

$$\frac{\partial \bar{q}}{\partial t}+\frac{\partial \bar{C}_{\mathrm{p}}}{\partial t}+\frac{\partial \bar{C}_{\mathrm{TBPHA}}}{\partial t}=D_{\mathrm{s}}\left(\frac{\partial^2 \bar{q}}{\partial r^2}+\frac{2}{r}\frac{\partial \bar{q}}{\partial r}\right)+D_{\mathrm{p1}}\left(\frac{\partial^2 \bar{C}_{\mathrm{p}}}{\partial r^2}+\frac{2}{r}\frac{\partial \bar{C}_{\mathrm{p}}}{\partial r}\right)+D_{\mathrm{p2}}\left(\frac{\partial^2 \bar{C}_{\mathrm{TBPHA}}}{\partial r^2}+\frac{2}{r}\frac{\partial \bar{C}_{\mathrm{TBPHA}}}{\partial r}\right) \quad (15)$$

where $\bar{C}_{\mathrm{TBPHA}}$ is the TBP–valeric acid complex concentration extracted by chemical reaction with TBP in the organic phase inside the particle pores and $\mathrm{D_{p2}}$ is its pore diffusivity.

The total valeric concentration inside the particle, $\bar{C}_{\mathrm{A}}$, can be expressed as:

$$\bar{C}_{\mathrm{A}}=\bar{q}+\bar{C}_{\mathrm{p}}+\bar{C}_{\mathrm{TBPHA}} \quad (16)$$

According to Eqs. (1) and (5), the local equilibrium between $\bar{q}$, $\bar{C}_{\mathrm{p}}$, and $\bar{C}_{\mathrm{TBPHA}}$ can be expressed by the following equations:

$$\bar{C}_{\mathrm{p}}=\left(\frac{\bar{q}}{k}\right)^{1/n}\varepsilon_{\mathrm{p}}(1-x) \quad (17)$$

$$\bar{C}_{\mathrm{TBPHA}}=K_{\mathrm{c}}\frac{\bar{C}_{\mathrm{TBPi}}(\bar{q}/k)^{1/n}}{1+K_{\mathrm{c}}(\bar{q}/k)^{1/n}} \quad (18)$$

where ε_{p} is the particle porosity and x is the fraction of the pore volume filled with the extractant, experimentally calculated from the impregnation results with values that are shown in Table 2.

Concentration of species inside the particle, $\bar{q}$, $\bar{C}_{\mathrm{p}}$, and $\bar{C}_{\mathrm{TBPHA}}$ can be estimated from Eqs. (16) through (18). It was found that valeric acid concentrations in the aqueous phase inside the particle, $\bar{C}_{\mathrm{p}}$, are very low, below 1.8% of the total valeric acid inside the particle were obtained in all experiments. Such a result may be due to the strong hydrophobicity of the Amberlite XAD-4 resin that increases with the addition of the water insoluble TBP. Therefore, the term that accounts for the diffusion of the undissociated valeric acid in the aqueous phase inside the pores was neglected in both models given by Eqs. (14) and (15) for experiments with fresh resin and with EIR, respectively.

Taking into account the above consideration, the combination of Eqs. (15) and (16) leads to the following equation:

$$\frac{\partial \bar{C}_{\mathrm{A}}}{\partial t} = \left[\left(D_{\mathrm{s}} + D_{\mathrm{p2}}\frac{d\bar{C}_{\mathrm{TBPHA}}}{d\bar{q}}\right)\frac{d\bar{q}}{d\bar{C}_{\mathrm{A}}}\right]\left(\frac{\partial^2 \bar{C}_{\mathrm{A}}}{\partial r^2} + \frac{2}{r}\frac{\partial \bar{C}_{\mathrm{A}}}{\partial r}\right) \tag{19}$$

Comparison of the parallel model, Eq. (19), with the well-known homogeneous model,[22] leads to the following equation for the effective diffusivity:

$$D_{\mathrm{e}}\frac{d\bar{C}_{\mathrm{A}}}{d\bar{q}} = \left(D_{\mathrm{s}} + D_{\mathrm{p2}}\frac{d\bar{C}_{\mathrm{TBPHA}}}{d\bar{q}}\right) \tag{20}$$

The terms $d\bar{C}_{\mathrm{A}}/d\bar{q}$ and $d\bar{C}_{\mathrm{TBPHA}}/d\bar{q}$ were calculated by derivation of Eqs. (16) through (18), taking into account values of parameters K_{c}, k, and n, shown in Table 1, and x values, shown in Table 2.

Figure 5 shows values of D_{e} $(d\bar{C}_{\mathrm{A}}/d\bar{q})$ vs. $d\bar{C}_{\mathrm{TBPHA}}/d\bar{q}$, where D_{e} was estimated with the homogeneous diffusion model. Its values are shown

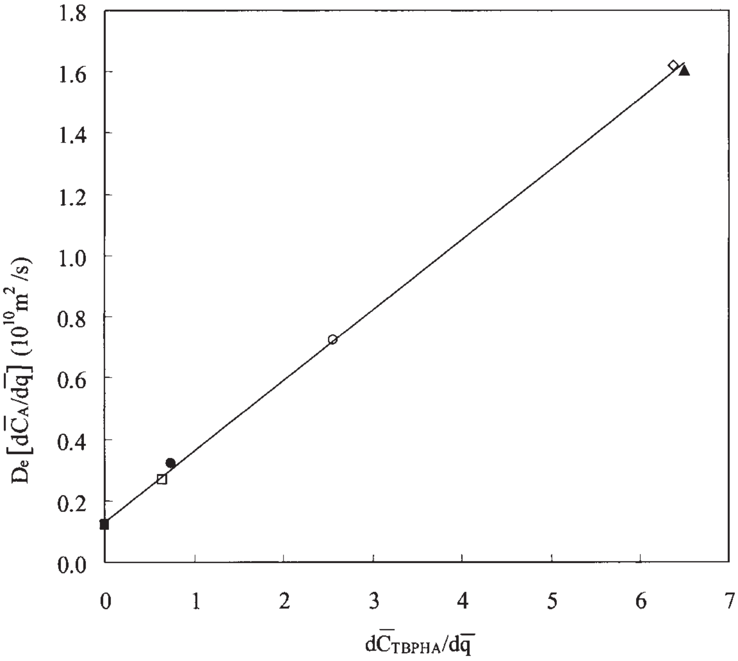

Figure 5. Linear fitting of Eq. (20) for the systems shown in Table 2: (◇), experiment *a*; (○), experiment *b*; (●), experiment *c*; (■), experiment *d*; (□), experiment *e*; (▲), experiment *f* (linear regression, $r = 0.999$).

in Table 2. From a linear fitting ($r = 0.999$) the following pore and surface diffusivities were obtained: $D_{p2} = 2.30 \times 10^{-11}\,\mathrm{m^2/s}$ and $D_s = 1.30 \times 10^{-11}\,\mathrm{m^2/s}$. This result shows that the pore and the surface diffusivities are of the same order of magnitude, indicating that both pore and surface diffusion have a similar contribution in the intraparticle diffusion process. It should be appreciated that the D_s value is very close to the D_e value estimated with the homogeneous model for the experiment *d* (without TBP).

CONCLUSION

The equilibrium and mass transfer rates of valeric acid from aqueous solutions with Amberlite XAD-4 and TBP–impregnated Amberlite XAD-4, were studied. The equilibrium data for the adsorption of valeric acid on Amberlite XAD-4 is described by a Freundlich isotherm. The concentration of TBP in the EIR increases with TBP concentration in the impregnating solution. The maximum concentration of TBP in the resin was $2.592\,\mathrm{mol\,TBP/dm^3}$ of fresh resin, beyond this concentration, the EIR becomes sticky and is not suitable for extraction purposes.

The amount of valeric acid extracted by the EIR was found to increase with the TBP concentration in the EIR. An equilibrium model, which considers the simultaneous adsorption by the resin and the reactive extraction by TBP inside the particle pores, provided a satisfactory correlation of experimental data. It was found that the valeric acid extraction rate was comparatively faster under the initial conditions of higher TBP concentration in the resin and lower valeric acid concentration in the aqueous phase. Fick's second law was used to correlate the mass-transfer data. A homogeneous diffusion model was applied to estimate the intarparticle effective diffusivities, D_e, being of the order of $10^{-11}\,\mathrm{m^2/s}$. Valeric acid concentration in the aqueous phase inside the particle pores was very low as a result of the strong hydrophobicity of the Amberlite XAD-4 resin, which increases as the water insoluble TBP is added.

A heterogeneous diffusion model taking into account pore diffusion of the TBP–valeric acid complex and solid surface diffusion of the valeric acid is suggested. From this model, it was found that pore and solid surface diffusivities were of the same order of magnitude ($10^{-11}\,\mathrm{m^2/s}$) and, hence, it can be considered that both pore and surface diffusion have a significant contribution to the intraparticle diffusional mass-transfer flux.

NOMENCLATURE

a = average radius of resin particle (dm).

C_{A} = analytical (total) concentration of the valeric acid in the aqueous phase (mol/dm^3).

C_{HA} = concentration of the undissociated valeric acid in the aqueous phase (mol/dm^3).

$\bar{C}_{\mathrm{A}}$ = molar concentration of the total valeric acid in the EIR (mol/dm^3 of fresh resin).

$\bar{C}_{\mathrm{p}}$ = molar concentration of the undissociated valeric acid in the aqueous phase inside the EIR pores (mol/dm^3 of fresh resin).

$\bar{C}_{\mathrm{TBP}}$ = molar concentration of the free extractant inside the EIR pores (mol/dm^3 of fresh resin).

$\bar{C}_{\mathrm{TBPHA}}$ = valeric acid concentration extracted by chemical reaction with TBP inside the EIR pores (mol/dm^3 of fresh resin).

D_{e} = intraparticle effective diffusivity in the EIR (dm^2/s).

D_{p1} = pore diffusivity of the undissociated valeric acid in the aqueous phase inside the particle pores (dm^2/s).

D_{p2} = pore diffusivity of the TBP–valeric acid complex in the organic phase inside the EIR pores (dm^2/s).

D_{s} = solid surface diffusivity of valeric acid adsorbed on the solid resin (dm^2/s).

HA = undissociated valeric acid.

k = Freundlich parameter in Eqs. (1) and (6) (mol$^{1\text{-}n}$ dm^{3n}/dm^3 of fresh resin)

K = equilibrium distribution ratio of the undissociated valeric acid, defined by Eq. (9) (dm^3/dm^3 of fresh resin).

K_{a} = dissociation constant of valeric acid (mol/dm^3).

K_{c} = chemical reaction constant defined by Eq. (4) (dm^3/mol).

M = amount of valeric acid sorbed in the EIR (mol).

n = Freundlich parameter in Eqs. (1) and (6).

$\bar{q}$ = concentration of valeric acid adsorbed in the solid phase of the resin (mol/dm^3 of fresh resin).

r = radial direction.

t = time (s).

TBP = tri-*N*-butyl phosphate.

TBPHA = valeric acid–TBP complex.

V = volume of aqueous phase (dm^3).

$\bar{V}$ = volume of resin (dm^3 of fresh resin).

x = pore fraction filled with the extractant.

α = dimensionless group, defined by Eq. (12).

ε_{p} = particle porosity.

Subscripts

i = initial.
S = aqueous samples withdrawn.

Superscript

(overbar) = resin phase.

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