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Nondispersive Extraction of Cr(VI) with Aliquat 336: Influence of Carrier Concentration

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ABSTRACT

Kinetic experiments on the extraction of Cr(VI) with Aliquat 336 performed in hollow fiber modules and in the 1% (v) $\leq$ Aliquat 336 $\leq$ 10% (v) and 10 g/m^3 $\leq$ Cr(VI) $\leq$ 500 g/m^3 range of concentrations have been successfully modeled by means of the integration of the mass conservation equation and associated boundary conditions. Different values of the mass transport coefficient through the organic membrane have been obtained depending on the total carrier concentration.

INTRODUCTION

The toxicity of industrial effluents containing chromium(VI) can be reduced by removal of the chromium with liquid–liquid extraction using quaternary ammonium salts as selective carriers in the organic phase.

Several works have reported the use of primary amines such as Primene JMT (1), secondary amines such as Adogen 382 and Adogen 283 (2), tertiary amines such as TOA (3–7), and Alamine 336 (8) for the extraction of Cr(VI). Quaternary ammonium salts have been shown to be very effective for the removal of chromate ion from wastewater, i.e., TOMAC (9, 10), Aliquat 26, Aliquat 221 (11), and Aliquat 336 (12–20).

Hollow fiber contactors present several advantages in comparison to the traditional mixer-settlers: namely, a very large interfacial area per unit

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extractor volume without direct mixing of the aqueous and organic phases, no need for a difference in phase densities, and no problems due to loading and flooding.

Working with the extraction of Cr(VI) with Aliquat 336 in hollow fiber modules in a previous work, the influence of the variables referred to the aqueous phase has been reported, i.e., initial concentration of Cr(VI) and linear velocity of the fluid phase on the kinetics of the extraction process. Following a similar procedure in this work, the kinetic analysis and modeling of the influence of the composition of the organic phase in the 1% (v) $\leq$ Aliquat 336 $\leq$ 10% (v), range to obtain the mass transport parameters is reported.

EXPERIMENTAL PROCEDURE

The experimental procedure and analytical methods were the same as those described in a preceding paper (20). The hollow fiber membrane module is formed by 3 microporous polypropylene fibers inserted in a glass shell. The shell consisted of a 4-mm-i.d., 7-mm-o.d., and 30 cm long glass tube with lateral openings at both ends to allow the circulation of the organic solution, while the feed aqueous solution circulates through the lumen of the fibers. Both inside and outside streams are driven by piston pumps. The outside stream comes from a magnetically stirred tank. The fibers were firmly epoxy bonded to the ends of the permeation shell.

Fibers with 0.6-mm-i.d., 1.0-mm-o.d., 0.5 μm d_{pore}, and $\epsilon = 63\%$ were supplied by ENKA, A.G.

To determine the influence of carrier concentration on the solute flux, the concentration of Aliquat 336 in the organic phase was varied in the 1% (v) to 10% (v) range. Kerosene was used as the diluent, and 5% (v) of (±)3,7-dimethyl-3-octanol was added in order to avoid the segregation of a gelatinous phase. The organic phase was continuously recycled with a linear velocity of 1.35×10^{-3} cm/s. The organic phase wetted the hollow fibers due to their hydrophobic character.

Feed solutions consisted of aqueous solutions of Na_2CrO_4 in the 10 g/m^3 $\leq$ Cr(VI) $\leq$ 500 g/m^3 concentration range. They flowed in a once-through operation mode through the lumen of the hollow fibers at a linear velocity of 5.9×10^{-3} m/s.

The pressure of the aqueous phase was maintained higher than the pressure of the organic phase, ensuring that no displacement of the organic phase from the pores of the hollow fiber took place. These solutions were collected at the module outlet, where samples were taken and prepared for analysis. A schematic diagram of the setup is shown in Fig. 1.

The Cr(VI) concentration was measured in a Perkin-Elmer 1100 B Absorption Spectrophotometer.

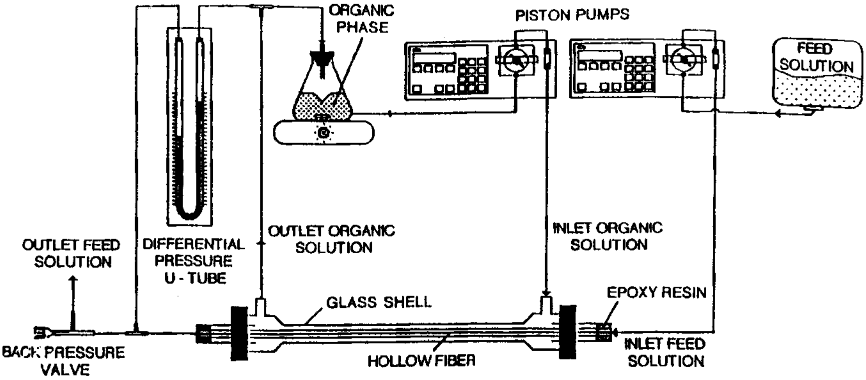

FIG. 1 Schematic diagram of the experimental set-up.

RESULTS AND DISCUSSION

To develop the model of the system for the steady-state mass conservation equation with the associated boundary conditions to the aqueous stream, some assumptions were made:

Axial diffusion is negligible compared to axial convection; the Peclet number is greater than 100.

Fully developed one-dimensional laminar flow in the fiber.

Chemical equilibrium can be described by the mass action law; the stoichiometric and equilibrium equations are

$$CrO_4^{2-} + 2(AQ)Cl \rightleftharpoons (AQ)_2(CrO_4) + 2Cl^- \qquad (1)$$

which is defined as

$$K_{eq} = \frac{[(AQ)_2(CrO_4)][Cl^-]^2}{[CrO_4^{2-}][(AQ)Cl]^2} \qquad (2)$$

Under the above assumptions, the steady-state mass conservation equation for the solute species through the inner side of the hollow fibers takes the form

$$2v\left[1 - \left(\frac{r}{R}\right)^2\right]\frac{\partial C}{\partial z} = D\frac{1}{r}\frac{\partial}{\partial r}\left[r\frac{\partial C}{\partial r}\right] \qquad (3)$$

with associated boundary conditions

$$\text{B.C.1: } C = C_0, \quad z = 0, \quad \text{all } r \qquad (4)$$

$$\text{B.C.2: } \frac{\partial C}{\partial r} = 0, \quad r = 0, \quad \text{all } z \tag{5}$$

$$\text{B.C.3: } -D\frac{\partial C}{\partial r} = \overline{K}s(\overline{C}_i - \overline{C}), \quad r = R, \quad \text{all } z \tag{6}$$

After substitution of the concentration terms of Eq. (2) as a function of the complex species at the interface, $\overline{C}_i$, and of the solute concentrations, C, rearrangment leads to

$$\overline{C}_i = \frac{4(C_0 - C)^2 + 4K_{eq}C\overline{C}_M - [2(C_0 - C)]\sqrt{4(C_0 - C)^2 + 8K_{eq}C\overline{C}_M}}{8K_{eq}C} \tag{7}$$

The numerical method used in the resolution of this system of partial differential equations was presented in an earlier paper (20). The computer program yielded values for the average radial concentration of Cr(VI) at the outlet of the module for different values of the solute–carrier complex concentration in the organic phase.

Figures 2–4 report the experimental results expressed as solute flux versus dimensionless chromium concentration in the organic phase corresponding to concentrations of Aliquat 336 of 10% (v), 5% (v), and 1% (v), respectively. The curves of Figs. 2–4 show a similar behavior with respect

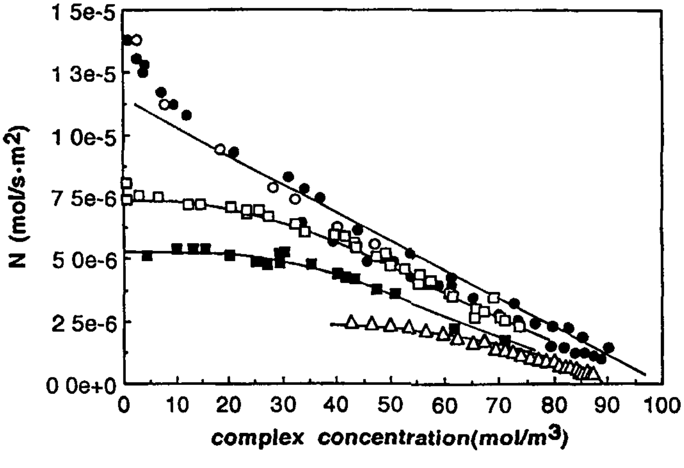

FIG. 2 Solute flux versus complex species concentration in the organic phase. 10% (v) Aliquat 336 and different C_0; (○) 500 g/m³, (●) 250 g/m³; (□) 150 g/m³, (■) 100 g/m³, (△) 50 g/m³.

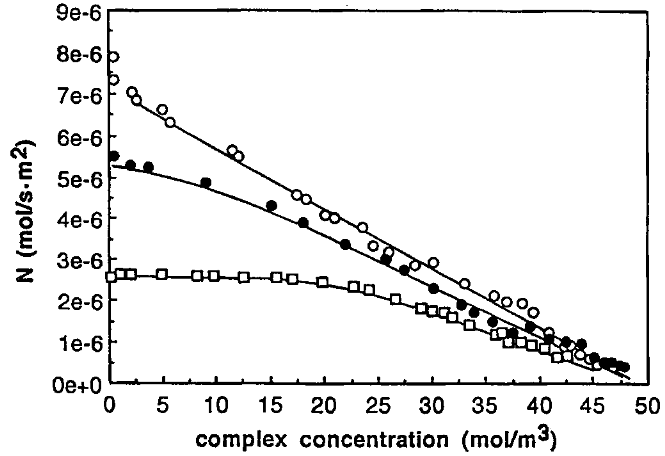

FIG. 3 Solute flux versus complex species concentration in the organic phase. 5% (v) Aliquat 336 and different C_0; (○) 150 g/m³, (●) 100 g/m³, (□) 50 g/m³.

to the kinetics of the system, i.e., there are three kinetic regimes as a function of the initial concentration of Cr(VI) for a given value of the concentration of Aliquat 336: 1) kinetic control of the mass transport in the aqueous phase (flat zone of the curves), 2) kinetic control of the mass transport through the membrane fiber wall (linear zone), and 3) an interme-

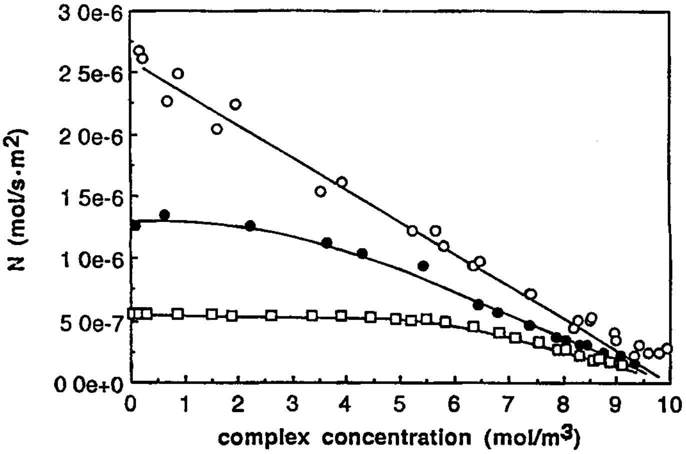

FIG. 4 Solute flux versus complex species concentration in the organic phase. 1% (v) Aliquat 336 and different C_0; (○) 50 g/m³, (●) 25 g/m³, (□) 10 g/m³.

diate region where the control is shared between the aqueous and the membrane phases.

Evaluation and optimization of the mass transport parameters was carried out according to the procedure described in a previous paper (20) where kinetic results obtained at a constant concentration of Aliquat 336 and variable Cr(VI) concentration and linear velocity of the aqueous phase were satisfactorily described by means of the integrated mass conservation equation.

To evaluate the mass transport coefficient through the organic membrane, it was noted that when the mass transport through the organic membrane governs the kinetic control, the kinetic expression for the solute flux is

$$N = \overline{K}s(\overline{C}_T - \overline{C}) \tag{8}$$

where $\overline{C}_T$ is the highest complex concentration at the interface (0.1, 0.05, or 0.01 M), $\overline{C}$ is the complex concentration in the organic solution, $\overline{K}$ is the membrane mass transfer coefficient, and s = 1.305, the shape factor of the hollow fibers. The mass transport coefficients corresponding to different values of the carrier concentration, Aliquat 336, have been determined from the slopes of the straight lines in Fig. 5. The resulting values are reported in Table 1.

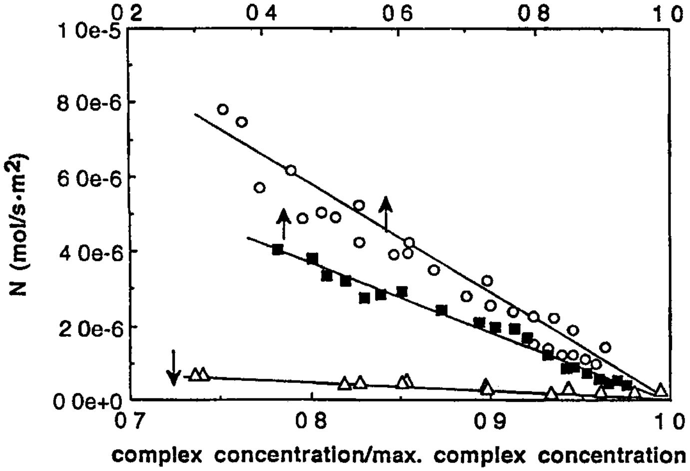

FIG. 5 Solute flux versus the adimensional concentration of the complex species in the organic phase: (○) 10% Aliquat 336-C_0 = 250 mg/L, (■) 5% Aliquat 336-C_0 = 150 g/m^3, (△) 1% Aliquat 336-C_0 = 50 g/m^3.

TABLE 1
Values of the Membrane Mass Transfer Coefficient, $\bar{K}$, at Different Concentrations of Aliquat 336

Concentration of Aliquat 336 (%)	$\bar{K}$ (cm/s)	r
10	8.08×10^{-6}	−0.969
5	1.06×10^{-5}	−0.989
1	2.28×10^{-5}	−0.939

There is a strong dependence of the total carrier concentration on the values of $\bar{K}$ with an important increase in the mass transport coefficient as the concentration of Aliquat 336 decreases. A similar behavior has been reported in the literature for different extraction systems, i.e., Babcok et al. (21) studied the extraction of uranium with Alamine 336 and observed an important decrease of the uranium flux for concentrations of the carrier above 30% which was attributed to a significant increase in the viscosity of the organic solution.

According to film theory, the mass transport coefficient is defined as

$$\bar{K} = D_{\text{eff}}/m \tag{9}$$

where D_{eff} is the effective diffusivity of the complex species and m is the effective pore length of the hollow fiber.

Most of the empirical correlations for the estimation of effective diffusivity in low pressure liquid systems are based on the Stokes–Einstein equation which implies that the diffusivity and the solvent viscosity are inversely related (22). That would imply a decrease in the mass transport coefficient, Eq. (9), with increasing viscosity (carrier concentration).

However, in systems where the organic solution containing the carrier compound is immobilized in the pores of a polymeric support, viscosity changes due to interactions with the solid wall must be considered (23), making the development of a mathematical expression able to predict the viscosity of the solution very difficult.

With the values of the mass transport coefficient through the organic membrane, given in Table 1, the integration of the set of differential equations, Eqs. (3)–(6), was carried out using K_{eq}, the equilibrium constant, as an adjustable parameter (20).

In an earlier work the diffusivity of the chromate anion in the aqueous phase, D, was found to be 2.3×10^{-5} cm^2/s (20). This value was estimated for working with a carrier concentration of 10%. The parameter D does

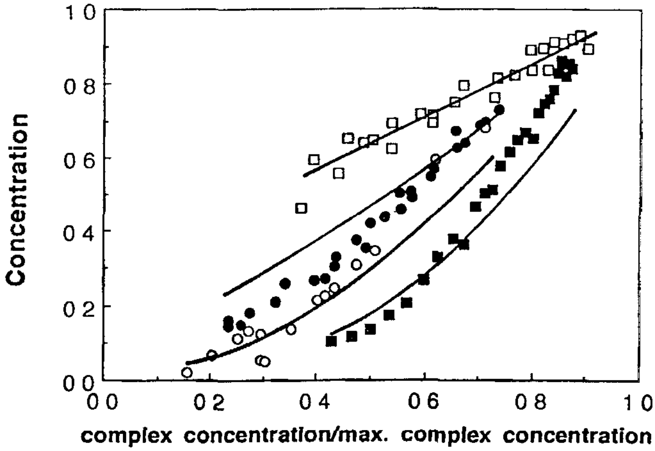

FIG. 6 Comparison between the simulated curves and the experimental results for 10% Aliquat 336 and different C_0; (□) 250 g/m^3, (●) 150 g/m^3, (○) 100 g/m^3, (■) 50 g/m^3.

not depend on the carrier concentration; therefore, in this work this value has been used in the simulation of the results at lower concentrations of the extractant (5 and 1% Aliquat 336) to determine the value of the equilibrium constant.

Figures 6–8 show comparisons between the experimental results expressed as a dimensionless concentration of Cr(VI) in the aqueous phase

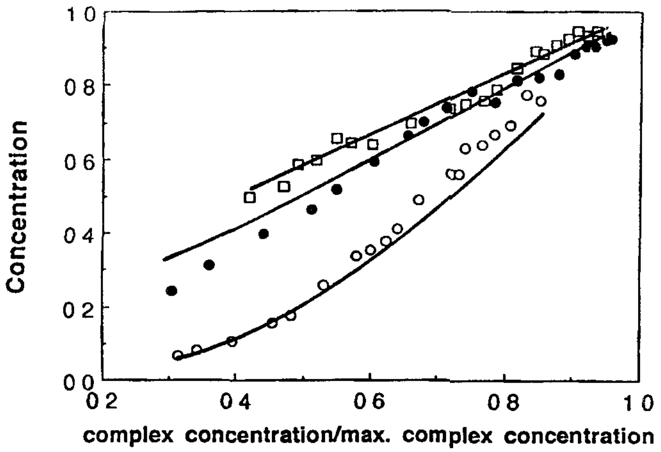

FIG. 7 Comparison between the simulated curves and the experimental results for 5% Aliquat 336 and different C_0; (□) 150 g/m^3, (●) 100 g/m^3, (○) 50 g/m^3.

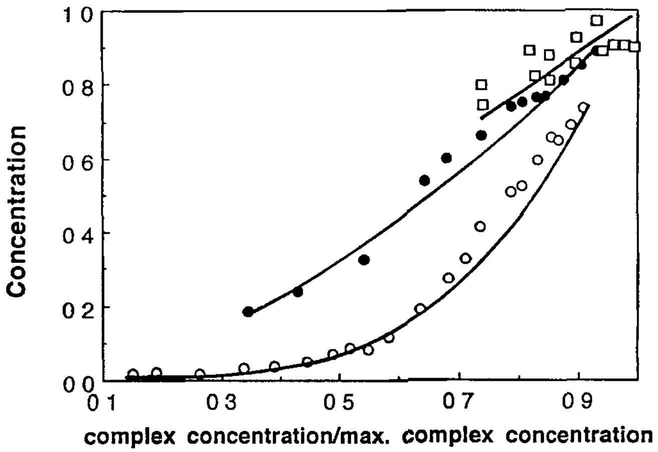

FIG. 8 Comparison between the simulated curves and the experimental results for 1% Aliquat 336 and different C_0; (□) 50 g/m^3, (●) 25 g/m^3, (○) 10 g/m^3.

vs a dimensionless concentration of complex species in the organic phase corresponding to a 10, 5, and 1% total concentration of Aliquat 336 in the organic phase and the simulated curves.

Table 2 reports the values of the optimized parameter K_{eq} as well as the values of the standard deviation from comparisons of experimental and simulated data of different values of the initial carrier concentration.

TABLE 2

Values of the Equilibrium Constant, K_{eq}, at Different Concentrations of Cr(VI) and Aliquat 336

Concentration of Aliquat 336 (%)	Initial concentration of Cr(VI) (g/m^3)	K_{eq}	σ
10	250	—	0.048
10	150	0.81	0.229
10	100	0.65	0.318
10	50	0.15	0.174
5	150	—	0.037
5	100	—	0.082
5	50	0.60	0.099
1	50	—	0.065
1	25	0.70	0.067
1	10	0.69	0.167

No sensitivity to the equilibrium constant was observed in the experiments governed by mass transport through the organic membrane. From the data of Table 2, it can apparently be assumed there is an average equilibrium constant, $K_{eq} \simeq 0.6$; however, an analysis based on a broader range of concentrations showed a dependence of this parameter on both the concentration of the aqueous and the organic species. Analyzing the simple reaction (AQ)chloride $\rightleftharpoons$ (AQ)hydroxide, Galan et al. (24) reported a successful model for the description of the chemical equilibrium by taking into account both the nonideality of the aqueous and the organic phases and using two fitting parameters.

CONCLUSIONS

This paper has applied the model presented previously by Alonso et al. (20) to analyze the influence of the carrier concentration on the extraction kinetics of chromium(VI) with Aliquat 336 in hollow fiber modules and in the 1% (v) $\leq$ Aliquat 336 $\leq$ 10% (v) range of concentrations. Kinetic experiments were described satisfactorily by the corresponding integrated conservation equation with associated boundary conditions.

Comparison between experimental and simulated results lead to the determination of the mass transport coefficient and the equilibrium constant. The values obtained for the mass transport coefficient through the organic membrane were highly dependent upon the total carrier concentration. This fact can be attributed to the influence of the viscosity of the organic phase on the diffusivity of the complex species through the same phase.

The values for the equilibrium constant were dependent on both the aqueous concentration of chromium(VI) and the organic concentration of Aliquat 336. Although the complexity of the exchange equilibria of different solutes with Aliquat 336 has been reported in the literature (24), in this work it was assumed that equilibrium can be described by the mass action law. This could explain the observed dependence of the equilibrium constant on the concentrations of the aqueous and organic species. Therefore, one way of to improve the model would be taking nonideality into account in the expression for equilibria.

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NOMENCLATURE

C	solute concentration in the aqueous phase (mol/m^3)
$\overline{C}$	solute–carrier complex equilibrium concentration in the organic phase (mol/m^3)
$\overline{C}_i$	solute–carrier complex equilibrium concentration at the fluid–membrane interface (mol/m^3)
$\overline{C}_M$	total carrier concentration in all forms (carrier and carrier–solute complex) (mol/m^3)
C_0	initial solute concentration in the aqueous phase (mol/m^3)
D	diffusivity of the solute in the aqueous phase (m^2/s)
D_{eff}	effective diffusivity of the complex species in the organic phase (m^2/s)
$\overline{K}$	membrane mass transfer coefficient (m/s)
K_{eq}	equilibrium constant defined by Eq. (2)
m	pore length (m)
N	solute flux (mol/s·m^2)
R	inner radius of the fiber (m)
R_e	outer radius of the fiber (m)
r	radial distance (m)
s	shape factor based on the inside surface area $[(R_e - R)/R \ln(R_e/R)]$
Sh_w	wall Sherwood number, $R\overline{K}s/D$
v	linear velocity of the aqueous phase (m/s)
z	axial distance (m)

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