Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Alonso, Ana I. , Galan, Berta , Irabien, Angel and Ortiz, Inmaculada(1997) 'Separation of Cr (VI) with Aliquat 336: Chemical Equilibrium Modeling', Separation Science and Technology, 32: 9, 1543 — 1555

To link to this Article: DOI: 10.1080/01496399708004065

URL: http://dx.doi.org/10.1080/01496399708004065

SEPARATION SCIENCE AND TECHNOLOGY, **32**(9), pp. 1543–1555, 1997

Separation of Cr(VI) with Aliquat 336: Chemical Equilibrium Modeling

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ABSTRACT

The separation of chromium(VI) from industrial wastewaters is of great interest mostly due to the high toxicity of this metal. Although the extraction of Cr(VI) with anionic extractants (and among them, quaternary ammonium salts) has been widely studied using different technologies, a suitable equilibrium model it has not been reported due to the complex behavior of the organic phase. In this work a general methodology for modeling of the chemical equilibrium of Cr(VI) is presented. Discrimination between mathematical models that take account of the nonideal behavior of the organic phase led to the selection of a one-parameter empirical function of the total extractant concentration, $K = K_c c_0^n$. The parameter values estimated for this model are the equilibrium constant ($Kp = 0.197$) and the fitting parameter ($n = 0.661$), and they are used in the expression for the description of the extraction equilibrium:

$$0.197 = \frac{[\mathrm{Cl}^-]^2[\overline{(\mathrm{AQ})_2\mathrm{CrO}_4}]}{[\mathrm{CrO}_4^{2-}][\overline{(\mathrm{AQ})\mathrm{Cl}}]^2}\, c_0^{066}$$

This equation can satisfactorily describe the experimental behavior of chromium(VI) extraction with Aliquat 336 and thus provides a useful expression that could be introduced into mathematical models directed toward the design and optimization of the separation process.

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INTRODUCTION

Solvent extraction processes have become an attractive alternative to traditional technologies for the removal of metals from waste effluents. Among these processes, nondispersive solvent extraction (NDSX) in hollow fiber modules has been shown to be one of the best options. NDSX in hollow fiber modules offers a very large interfacial area per unit equipment volume without dispersion, it can be easily operated, and it allows for the simultaneous recovery and concentration of metals. The establishment of this technology as a new process depends very much on having reliable design models. For that reason, research efforts in the development of these processes should be directed toward the realization of suitable design models and parameters.

In selective NDSX the solute diffuses through the aqueous phase and reacts with the extractant at the interface placed in the pores of hollow fibers, resulting in the formation of a complex specie, an extractant-solute. Then this complex diffuses first through the organic liquid occupying the membrane pores and second through the organic phase in the shell side of the module. Consequently, it is essential to consider diffusion of solute through the boundary layers of the two phases in addition to the diffusion through the pores and the reversible chemical reaction at the interface.

Analysis of the mass transfer in these systems requires mathematical expressions describing concentration gradients where interfacial concentrations, i.e., concentrations at the interface between aqueous and organic solutions, have to be included (1–4). Extraction systems involving ionic species are generally thought to reach chemical equilibrium at the interface, and thus concentrations at the interface are usually related through equilibrium models of the chemical reactions. Consequently, mass transfer accompanied by chemical equilibirum has to be modeled in order to carry out simulation and design of the nondispersive extraction processes.

Therefore, to obtain mathematical models able to describe the behavior and performance of these processes, it is first necessary to elucidate the solute extraction mechanism leading to the description of the chemical equilibrium.

The removal of Cr(VI) from industrial wastewaters is of great interest mostly due to the high toxicity of chromium(VI) compounds. During recent years the application of different solvent extraction technologies to chromium removal and concentration has been widely studied; conventional liquid–liquid extraction (5), emulsion liquid membranes (6, 7), supported liquid membranes (8, 9), and nondispersive extraction (1, 3, 4, 10) are some of the new alternatives reported in the literature.

Although the complexity of the extraction behavior of quaternary ammonium salts is well known, in past equilibrium models for the extraction of chromium(VI) with Aliquat 336 (quaternary ammonium salt), the ideality of both the aqueous and organic phases has been considered, and so an equilibrium constant defined through the mass action law has been introduced. In the work reported by Alonso et al. (1), different values of the equilibrium constant for the extraction of Cr(VI) with Aliquat 336 were necessary in order to explain the system behavior under different experimental conditions. Therefore, the assumption of ideal behavior of the liquid phases in the results of that work is not accurate enough to describe the performance of the system, and thus a more reliable equilibrium expression should be used.

Several approaches have been reported in the literature in order to explain the equilibrium results of different extraction systems using Aliquat 336 as the extractant. Calvarin et al. (11) described the extraction of cyanocobalamin cyanide with Aliquat 336 by an empirical ideal associated solution model assuming aggregation of species in the organic phase. A similar method was followed by Mizelli and Bart (12) to explain the reaction between dicyandiamide and cyanamide with Aliquat 336. A different approach to the description of extraction of nitric acid from ammonium nitrate solutions by Aliquat 336 nitrate which considered nonideality in both the aqueous and organic phases was used by Černá and coworkers (13). In a different study on the system Cr(VI)–Aliquat 336, Salazar et al. (7) proposed a semiempirical model for the chromate exchange reaction while working with low concentrations of Aliquat 336 [0.5% (v/v)], but the utility of that model was restricted to a very limited range of experimental conditions.

Following the nonideality approach, the study of the Aliquat chloride $\leftrightarrows$ Aliquat hydroxide equilibrium as a test system was carried out by Galan et al. (14). In that work the extraction was modeled by taking into account the nonideal behavior of both liquid phases and using an empirical expression for the activity coefficients in the organic phase as a function of the extractant molar fraction.

Based on a systematic method developed in previous work (14), analysis and modeling of the liquid–liquid equilibrium of Cr(VI) with Aliquat 336 has been carried out.

The purpose of this study is to develop an accurate expression to describe and simulate the interfacial concentrations of the species involved in the extraction of Cr(VI) with Aliquat 336 as a necessary part in the development of a mathematical model for the extraction of Cr(VI) with Aliquat 336 by NDSX in hollow fiber modules.

EXPERIMENTAL

Aqueous solutions of chromium(VI) were prepared by dissolving sodium chromate (analytical-grade Fluka) in water. The chromium initial concentration was in the 100 to 1000 mg/L range. All aqueous solutions were analyzed by atomic absorption spectrometry using standard techniques.

Aliquat 336, a mixture of trialkylmethylammonium chlorides (Fluka), was used as received to prepare 1, 10, and 30% (v/v) solutions in kerosene (Petronor S.A.). A modifier, isodecanol (Exxon), was added to all organic solutions in order to avoid the segregation of a third (second organic) phase. Its concentration was 5% (v/v) in every case.

Extraction studies were carried out in a rotatory SBS stirrer (5–150 rpm). Volumes of the aqueous and organic solutions in range ratios of 1/10 to 5/1, aqueous volume/organic volume, were shaken for 90 minutes. This period of time was chosen to insure complete equilibration of the two phases. All the experiments were conducted at a temperature of 20 ± 1°C. The equilibration was carried out in the dark to avoid photochemical reduction of chromium(VI) (15). After equilibration, the phases were separated by centrifugation, and a sample of the aqueous phase was taken for chromium analysis. A new aqueous solution was equilibrated with the remaining organic phase while keeping the volume ratio constant; the process was repeated until the organic phase was saturated.

TABLE 1
Experimental Conditions and Estimated Equilibrium Constant for Different Initial Cr(VI) Concentrations and 10% (v/v) Aliquat 336

Exp.	Aliquat 336 concentration % (v/v)	Initial chromium concentration (mg/L)	Volume ratio, V_{aq}/V_{org}	Number of contacts	K_c
a	30	1000	3/1	9	
b	30	500	1/1	45	
c	10	1000	3/4	20	0.55
d	10	500	5/1	14	0.53
e	10	500	1/1	27	0.56
f1	10	100	4/1	13	0.60
f2	10	100	4/1	9	
g	1	500	1/10	33	
h	1	1000	1/1	8	

Experiments in a wide range of concentration were carried out in order to study the influence of both aqueous and organic concentrations on the equilibrium. Table 1 shows the experimental conditions.

RESULTS AND DISCUSSION

Chromium(VI) can present the following ions in aqueous solution: $HCrO_4^-$, CrO_4^{2-}, $Cr_2O_7^{2-}$, $HCr_2O_7^-$. The amount of each ion is influenced by the acidity and concentration of the solution. For concentrations of chromium (VI) between 100 and 1000 mg/L and pH values around 8, the CrO_4^{2-} ion is predominant (16). Chromium(VI) is taken up from aqueous solutions through anion exchange of CrO_4^{2-}, and the species $(AQ)_2CrO_4$ is formed in the organic solution (17). Therefore, extraction of chromium(VI) with Aliquat 336 can be described by the following reaction:

$$CrO_4^{2-} + 2\overline{(AQ)Cl} \leftrightarrows \overline{(AQ)_2CrO_4} + 2Cl^-$$

characterized by the equilibrium constant

$$K = K_cK_a = \frac{[Cl^-]^2[\overline{(AQ)_2CrO_4}]}{[CrO_4^{2-}][\overline{(AQ)Cl}]^2}\,\frac{\gamma_{CI}^2\gamma_C}{\gamma_S\gamma_E^2} \tag{1}$$

where γ is the activity coefficient and the subscripts S, CI, C, and E correspond to solute, contranion, complex species, and extractant, respectively.

The equilibrium concentrations obtained under conditions specified in Table 1 are shown in Figs. 1, 2, and 3.

As a preliminary approach, ideal behavior of the system was assumed ($K_a = 1$). Therefore $K = K_c$ and the model dimensionless equations were as follows.

Equilibrium constant expression:

$$K = \frac{C_{CI}^2C_C}{C_SC_E^2} \tag{2}$$

Extractant mass balance:

$$CT = C_E + 2C_C \tag{3}$$

Complex and contranion equilibrium dimensionless concentrations according to the stoichiometry:

$$C_C = C_{C_o} + (1 - C_S)RV \tag{4}$$

$$C_{CI} = 2(1 - C_S) \tag{5}$$

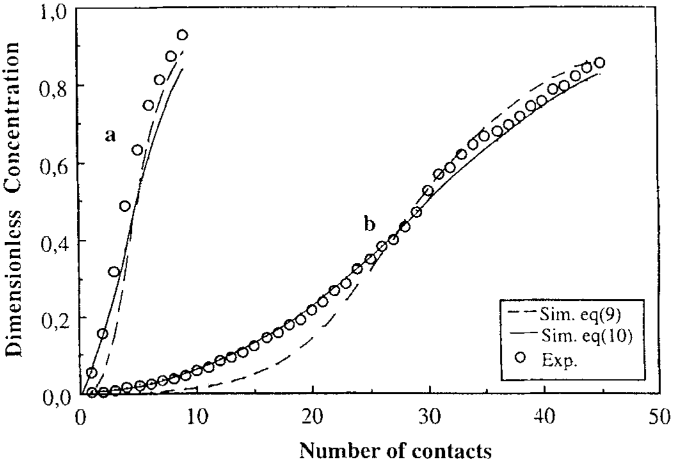

FIG. 1 Simulated (Eqs. 9 and 10) and experimental chromium concentration at successive contacts when 30% (v/v) Aliquat 336 was used (Experiments a and b).

RV is the volume ratio (aqueous volume/organic volume), *CT* is the total dimensionless concentration of extractant (complex and free extractant), and C_{Co} is the initial complex dimensionless concentration in each contact.

This one-parameter mathematical model was compared to experimental data using the SPEEDUP simulator in order to estimate preliminary con-

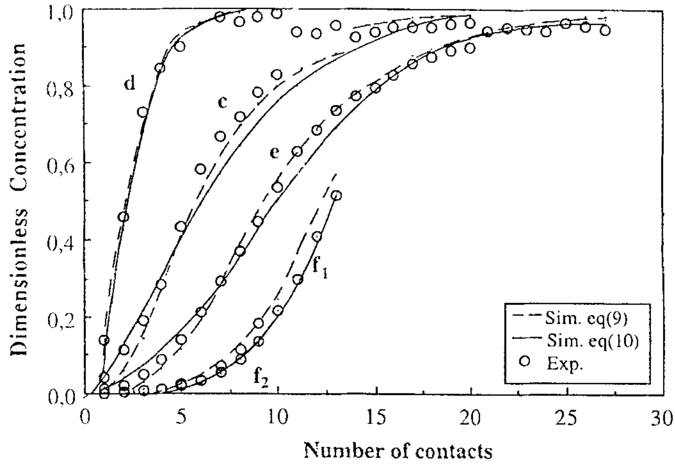

FIG. 2 Simulated (Eqs. 9 and 10) and experimental chromium concentration at successive contacts when 10% (v/v) Aliquat 336 was used (Experiments c, d, e, f1, and f2).

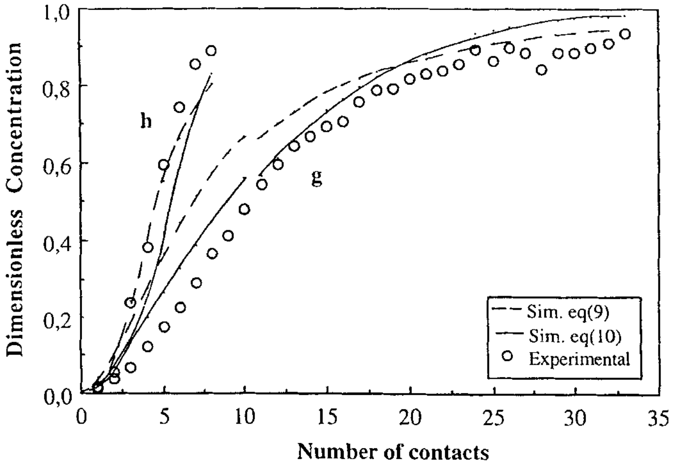

FIG. 3 Simulated (Eqs. 9 and 10) and experimental chromium concentration at successive contacts when 1% (v/v) Aliquat 336 was used (Experiments g and h).

stant equilibrium values. SPEEDUP is an equation-oriented process-simulation system that can be used for both steady-state and dynamic simulation of chemical processes. It also includes facilities for the optimization of process conditions and estimation of parameters. It allows equations, procedures, or arbitrary combinations of both to describe the process to be simulated.

The procedure consists of the resolution of the model equations for each successive contact taking into account every time that the initial organic concentration is the equilibrium concentration of the previous contact. The estimation of equilibrium parameters has been made from comparison between the experimental and simulated equilibrium Cr(VI) concentration based on the minimum value of the sum of the quadratic difference.

Table 1 shows the estimated values of the equilibrium constant, K_c, for different values of the initial concentrations of chromium(VI) in the aqueous feed when 10% (v/v) Aliquat 336 was used as extractant. It is observed that the values of the equilibrium constant obtained show slight variations that lie in the experimental range of error; thus, an ideal behavior of the aqueous phase was verified and is considered in the following analysis.

However, estimation of the equilibrium constant for different Aliquat 336 concentrations, Table 2, led to the conclusion that a nonideal behavior of the organic species involved in the extraction reaction ought to be taken into account in the equilibrium expression.

TABLE 2
Estimated Equilibrium Constant for Different Aliquat 336 Initial Concentrations

Exp.	Aliquat 336 concentration % (v/v)	K_c
a, b	30	0.28
c, d, e, f1, f2	10	0.58
g, h	1	2.66

A logarithmic fitting of K_c values to the total concentration of Aliquat 336 was performed with the data of Table 2. It led to the following equation:

$$\ln K_c = -1.6104 - 1.5234 \log[(\overline{\mathrm{AQCl}})]_0; \qquad r^2 = 1.000 \tag{6}$$

Considering that $K = K_c\,(\gamma_{\mathrm{C}}/\gamma_{\bar{\mathrm{E}}}^2)$, the ratio of the activity coefficients of the species in the organic phase, $\gamma_{\mathrm{C}}/\gamma_{\bar{\mathrm{E}}}^2$, could be expressed as a function of the total extractant concentration CT.

Therefore, in order to include the influence of the organic phase activity coefficients in the equilibrium model, two empirical expressions have been proposed.

1. Following the approach made by Galan et al. (14), a mathematical expression as a function of the extractant molar fraction was checked:

$$\ln \frac{\gamma_{\mathrm{C}}}{\gamma_{\bar{\mathrm{E}}}^2} = A\,\frac{C_{\mathrm{E}}}{CT} \tag{7}$$

2. An empirical expression resulting from the fit of the equilibrium constant to the extractant initial concentration:

$$\gamma_{\mathrm{C}}/\gamma_{\bar{\mathrm{E}}}^2 = c_0^n \tag{8}$$

Substituting Eq. (7) to (8) into Eq. (1) and considering ideal behavior of the aqueous phase on the equilibrium constant, the following equilibrium expressions can be written:

1. $$K = K_c \exp\left(A\,\frac{C_{\mathrm{E}}}{CT}\right) = \frac{C_{\bar{\mathrm{C}}\mathrm{l}}^2 C_{\mathrm{C}}}{C_{\mathrm{S}} C_{\bar{\mathrm{E}}}^2} \exp\left(A\,\frac{C_{\mathrm{E}}}{CT}\right) \tag{9}$$

2. $$K = K_c c_0^n = \frac{C_{\bar{\mathrm{C}}\mathrm{l}}^2 C_{\mathrm{C}}}{C_{\mathrm{S}} C_{\bar{\mathrm{E}}}^2}\, c_0^n \tag{10}$$

and two mathematical models can be obtained with the set of Eq. (2) to (5) with Eq. (2) substituted by Eqs. (9) and (10), respectively.

Following a similar procedure as described previously, the estimation of the model parameters A and K in the first model and n and K in the second model was carried out using SPEEDUP.

Comparison of all the experimental data obtained working with different initial aqueous and organic concentrations (Experiments a, b, c, d, e, f1, f2, g, h) with the simulated data for both models led to the following parameter values:

1. $A = -2.66$ (standard deviation = 0.42);
   $K = 2.47\text{E-}1$ (standard deviation = 0.43E-1)
2. $n = 0.66$ (standard deviation = 0.05);
   $K = 1.97\text{E-}1$ (standard deviation = 0.21E-1)

with a relative deviation defined as

$$s = \sqrt{\frac{\sum (C_{\text{sim}} - C_{\text{exp}})^2}{N - 1}} \tag{11}$$

equal to 6.18% and 5.00%, respectively.

The results of the numerical simulation are given in Figs. 1, 2, and 3 when the Aliquat 336 concentration was 30, 10, and 1%, respectively. From these Figures it can be observed that both models are in good agreement with the experimental results but that the second one fits the experi-

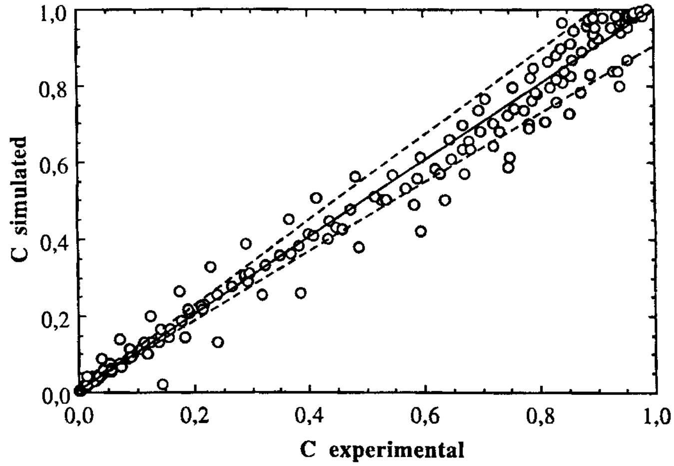

FIG. 4 Parity graph.

mental results in a slightly better way and shows a smaller value of the relative deviation (5.0% against 6.18%).

Figure 4 shows the parity graph for all the chromium(VI) dimensionless equilibrium concentrations modeled by the expression given by Eq. (10) where the equilibrium constant K_e is a function of the total extractant concentration. As 65% of the points lie within the 5% limits, 80% within 10% limits, and 89% within 15% limits (mean relative deviation of 5.00%), the fit of the model can be considered satisfactory in order to use this equilibrium expression for design purposes of mass transport processes in the research range of variables.

CONCLUSIONS

The liquid–liquid extraction equilibrium of Cr(VI) with Aliquat 336 has been experimentally studied and modeled. When ideal behavior of both phases was considered, similar values of K_c, around 0.58, for different initial concentrations of Cr(VI) and 10% (v/v) of Aliquat 336 were obtained. On the other hand, calculations yielded different values of K_c for different concentrations of Aliquat 336 (30%: $K_c = 0.28$; 10%: $K_c = 0.58$; 1%: $K_c = 2.66$). These estimated values of the equilibrium constant led to the conclusion that in the range of concentrations studied, ideal behavior can be contemplated only in the aqueous phase. The influence of activity coefficients must be considered in the organic phase.

Thus, two extraction models which take into account the nonideal behavior of the organic phase by means of empirical expressions have been proposed:

1. $$\ln \frac{\gamma_C}{\gamma_E^2} = A \frac{C_e}{CT} \tag{14}$$

2. $\gamma_C/\gamma_E^2 = c_0^n$ (fit of the experimental equilibrium constant to the total concentration of extractant).

Working with SPEEDUP simulator and from a comparison between experimental and simulated data and using the minimum summary of quadratic differences as the criterion, the values of the model parameters have been determined and discrimination between the models has been carried out. Both models lead to simulated results in good agreement with experimental results, but the model describing the ratio of activity coefficients of the organic species as a function of the total extractant concentration describes the performance of the extraction system slightly better.

The parameter values estimated for this model are $K = 0.197$ for the equilibrium constant and $n = 0.66$ for the fitting parameter. The equilibrium expression is therefore

$$0.197 = \frac{C_{\mathrm{Cl}}^2 C_{\mathrm{C}}}{C_{\mathrm{S}} C_{\mathrm{E}}^2} c_0^{0.66}$$

It is concluded that equilibrium models describing the nonideality of the organic phase through mathematical expressions as a function of the total extractant concentration or the extractant molar fraction can satisfactorily describe the experimental behavior of the chromium(VI) extraction with Aliquat 336. They should be introduced into mathematical models for the simulation and design of solvent extraction processes.

NOTATION

A	fitting parameter in Eq (9)
c_0	initial concentration of extractant in the organic phase (mol/l)
C_{S}	solute dimensionless concentration in the aqueous phase, $[\mathrm{CrO_4^{2-}}]/[\mathrm{CrO_4^{2-}}]_0$
C_{Cl}	contranion dimensionless concentration in the aqueous phase $[\mathrm{Cl^-}]/[\mathrm{CrO_4^{2-}}]_0$
C_{E}	extraction dimensionless concentration in the organic phase, $[\overline{\mathrm{AQCl}}]/[\mathrm{CrO_4^{2-}}]_0$
C_{C}	solute–extractant complex dimensionless concentration in the organic phase. $[\overline{\mathrm{(AQ)_2CrO_4}}]/[\mathrm{CrO_4^{2-}}]_0$
CT	total dimensionless concentration of extractant in the organic phase, $[\overline{\mathrm{AQCl}}]_0/[\mathrm{CrO_4^{2-}}]_0$
$C_{\mathrm{C}0}$	initial solute–extractant complex dimensionless concentration in the organic phase at each contact, $[\overline{\mathrm{(AQ)_2CrO_4}}]_0/[\mathrm{CrO_4^{2-}}]_0$
K	equlibrium constant defined by Eq. (1)
K_c	concentration function in equilibrium constant
K_a	activities coefficients function in equilibrium constant
n	fitting parameter in Eq. (10)
RV	volume ratio, aqueous volume/organic volume
s	standard deviation defind by Eq. (11)

Greek Letters

γ_{S}	solute activity coefficient in the aqueous phase
γ_{Cl}	contranion activity coefficient in the aqueous phase
γ_{E}	extractant activity coefficient in the aqueous phase

γ_C solute–extractant complex activity coefficient in the aqueous phase

ACKNOWLEDGMENT

Financial support from the Spanish CICYT(MEC) under project AMB93-0316 is gratefully acknowledged.

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Received by editor August 8, 1996
Revision received November 1996