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

Bulk Liquid Membrane for the Recovery of Chromium(VI) from a Hydrochloric Acid Medium Using Dicyclohexano-18-crown-6 as Extractant-Carrier

A. Zouhri[a]; B. Ernst[b]; M. Burgard[a]
[a] UNIVERSITÉ IBNOU ZOHR, AGADIR, MOROCCO [b] LABORATOIRE DE CHIMIE MINÉRALE ET ANALYTIQUE, UMR 7512 CNRS, STRASBOURG, CEDEX, FRANCE

To cite this Article Zouhri, A. , Ernst, B. and Burgard, M.(1999) 'Bulk Liquid Membrane for the Recovery of Chromium(VI) from a Hydrochloric Acid Medium Using Dicyclohexano-18-crown-6 as Extractant-Carrier', Separation Science and Technology, 34: 9, 1891 — 1905

To link to this Article: DOI: 10.1081/SS-100100745

URL: http://dx.doi.org/10.1081/SS-100100745

SEPARATION SCIENCE AND TECHNOLOGY, **34**(9), pp. 1891–1905, 1999

Bulk Liquid Membrane for the Recovery of Chromium(VI) from a Hydrochloric Acid Medium Using Dicyclohexano-18-crown-6 as Extractant-Carrier

A. ZOUHRI
FACULTÉ DE SCIENCES
UNIVERSITÉ IBNOU ZOHR
AGADIR, MOROCCO

B. ERNST and M. BURGARD*
LABORATOIRE DE CHIMIE MINÉRALE ET ANALYTIQUE
UMR 7512 CNRS
ECOLE EUROPÉENNE DE CHIMIE, POLYMÈRES ET MATÉRIAUX DE STRASBOURG
25 RUE BECQUEREL, 67087 STRASBOURG, CEDEX, FRANCE

ABSTRACT

The solvent extraction and transfer of chromic acid from hydrochloric acid medium through a bulk liquid membrane containing dicyclohexano-18-crown-6 (L) were studied. Extraction experiments pointed out that chromium(VI) was coextracted with the chloride ion which formed the complex ion pair $L(H_3O^+)CrO_3Cl^-$ in the organic phase. The Donnan equilibrium isotherm based on the extraction, stripping, and CrO_3Cl^- hydrolysis equilibria allowed prediction of the performance of the semipermeable membrane to concentrate chlorochromic acid in the receiving phase. Transport experiments confirmed the ability of the liquid membrane to recover chlorochromic acid in pure water. The transport kinetics was modeled by using the two-film theory applied to the liquid membrane.

Key Words. Liquid membrane; Chromium; Extraction; Transport; Dicyclohexano-18-crown-6

---

* To whom correspondence should be addressed. E-mail: burgard@chimie.u-strasbg.fr

www.dekker.com

INTRODUCTION

The removal of toxic metals from industrial wastewater is a major concern. Hexavalent chromium receives particular attention because of its high toxicity and its numerous industrial applications (electroplating, metal finishing, and corrosion inhibition) (1). Plating baths in the electroplating process contain 100–200 $g \cdot L^{-1}$ of hexavalent chromium (2), and they can be polluted by metallic cations (i.e., Fe^{3+}, Cr^{3+}, Ni^{2+}) of low concentration (1 to 10 $g \cdot L^{-1}$) and by anions (nitrates, chlorides, phosphates, sulfates). The rinsing waters used after chromium plating [concentration of chromium(VI) between 100 and 500 $mg \cdot L^{-1}$] need to be treated (<1 $g \cdot L^{-1}$) before discharge to the environment (3).

The treatment of electroplating effluents generally consists in a reduction of Cr(VI) to Cr(III) with a chemical reducing agent such as ferrous sulfate, sulfur dioxide, or sodium bisulfite, and then precipitation of the trivalent chromium as hydrated oxides. Other recycling processes involve anionic-exchange resins which are used to remove chromate or dichromate followed by elution with NaOH solution, and reverse osmosis. These techniques are costly and produce additional sludges. The possibility of recovering and concentrating chromium(VI) for reuse makes the techniques of liquid–liquid extraction and transport through a liquid membrane very attractive. Amine compounds [tri-*n*-octylamine (4, 5), triisooctylamine (6, 7)] and quaternary ammonium salts [trialkylmethylammonium salts (8–12)] have been the main extractants mentioned in the literature for the removal of chromium(VI). The stripping process with these compounds requires a reagent in the aqueous phase [e.g., NaOH for the amines (5) and chloride ions for the quaternary ammonium (12)]. In this case, chromium is recovered as chromic salts. The use of less basic extractants with the ability to solvate the hydrogen ion must be considered for a direct recovery of chromic acid. Neutral extractants such as tributyl phosphate (13, 14), trioctylphosphine oxide (15), 3-(4-pyridyl)-1,5-diphenyl pentane (16), 5-(4-pyridyl)nonane *N*-oxide (17), and crown ethers (18, 19) have been investigated for this purpose.

In previous work (19) we have showed that dicyclohexano-18-crown-6 (DC18C6) was the most efficient and selective extractant carrier of chromic acid for removal from a sulfuric medium compared with tributyl phosphate (TBP), dibutyl carbitol (Butex), and trioctylphosphine oxide (TOPO). It was also found that chromium(VI) was extracted as $HCr_2O_7^-$.

In this work, chromium(VI) extraction from a hydrochloric acid medium by an organic phase containing DC18C6 as well as stripping with pure water are investigated in order to predict the semipermeable character of the corresponding liquid membrane. Transfer kinetic experiments are presented and modeled using the two-film theory.

EXPERIMENTAL

Materials

Dicyclohexano-18-crown-6 (DC18C6) is a commercial mixture of the *cis syn cis* and *cis anti cis* isomers (ACROS Organics, 98%) and was used as the extractant without further purification. Dichloromethane (Carlo Erba 99.8%) was washed with distilled water in order to remove the stabilizer (0.2% ethanol). The aqueous phase of chromic acid was prepared using chromic oxide (CrO_3) (Prolabo 99%) diluted in hydrochloric acid (2 M) (SDS).

Extraction and Stripping Procedures

The liquid–liquid extraction experiments were carried out at room temperature in separatory funnels by shaking equal volumes of the aqueous and organic phases (45 mL each). The shaking time was fixed at 6 minutes in order to reach equilibrium. The initial concentration of Cr(VI) in the aqueous hydrochloric acid solution extended from 5×10^{-5} M (2.6 $mg \cdot L^{-1}$) to 1.5×10^{-2} M (2.6 $g \cdot L^{-1}$). The DC18C6 was diluted in various concentrations of dichloromethane (0.005, 0.01, and 0.02 M).

The organic and aqueous phases were divided after extraction. For the stripping step, each organic phase saturated in chromic acid (40 mL) was placed in contact with 2 mL of water in a separatory funnel (shaking time: 6 minutes).

Transport Experiments

The transport experiments were performed using a specific device shown by Fig. 1 (20). This device is particularly adapted to diluents more dense than the aqueous phase. It is composed of a 80-mm diameter glass cell thermostated at 298 ± 1 K where the organic phase (250 mL) is set in the bottom and a 45-mm diameter concentric bell cylinder separates the outer aqueous phase (feed phase I: 50 mL) from the inner aqueous phase (stripping phase II: 50 mL). A synchronous motor (Heidolph RZR 2000) is connected to the bell cylinder to stir the phases (200 rpm). The surface areas of the interfaces are assumed to be constant and equal to the areas of the nonagitated interface areas (between aqueous I and organic phase: $S_1 = 0.314$ dm^2; between organic and aqueous II phases: $S_2 = 0.159$ dm^2). In Experiment I the feed solution (50 mL) consisted of aqueous hydrochloric acid (2 M) with an initial Cr(VI) concentration of 0.05 M. In Experiment II a peristaltic pump (DEGASA, Heidelberg)

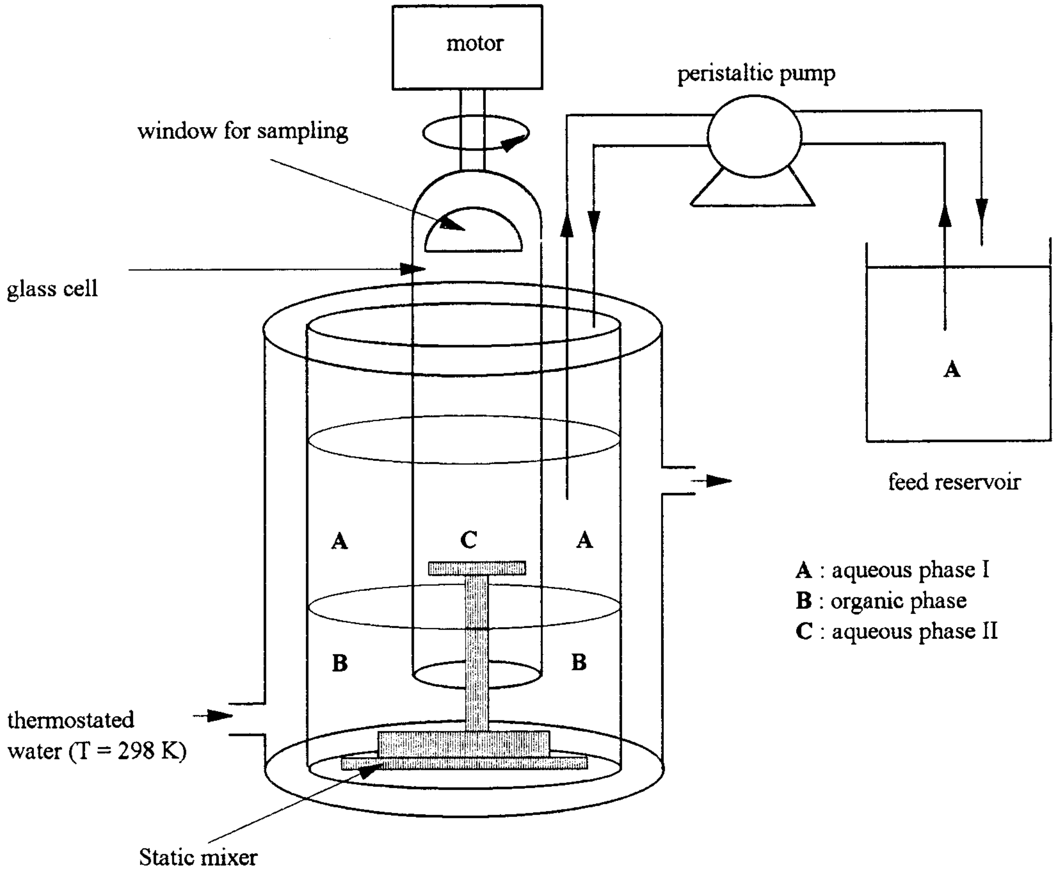

FIG. 1 Experimental setup for the transport rate measurements.

allowed circulation of the carrier solution of chromic acid (1 L) in order to keep a constant concentration value during the experiment [initial Cr(VI) concentration: 0.01 M].

Analysis

The chromium(VI) concentration was carried out in the liquid phase using a Perkin-Elmer UV-Visible spectrophotometer model 2380. The Cr(VI) species in the organic and aqueous phases were analyzed by quantitatively stripping the CrO_4^{2-} ions (wavelength: 370 nm, pH 11) with a 0.01 M potassium hydroxide solution. Basic solutions (pH $>$ 11) obtained by dissolving potassium chromate (K_2CrO_4) in a potassium hydroxide solution (0.01 M) with various concentrations of Cr(VI) (10^{-5} M to 2×10^{-4} M) were used as reference solutions.

The chloride ion concentrations were measured in the organic phase by ionic chromatography.

RESULTS AND DISCUSSION

Extraction of Chromic Acid in Hydrochloric Acid

The chromate ions react in an aqueous chloride medium (2 M) by forming the trioxochlorochromate(VI) ion (CrO_3Cl^-) (21–25) according to

$$HCrO_4^- + Cl^- + H^+ \rightleftharpoons CrO_3Cl^- + H_2O$$

The trioxochlorochromate(VI) ion was identified as the extracted species in the extraction of chromium(VI) from hydrochloric acid medium by tri-*n*-butyl phosphate (13), but it was not recognized in chromium(VI) extraction from chloride medium by triisooctylamine (6).

A recent study (18) on chromium(VI) extraction by DC18C6 indicates the existence of a Cr(VI):DC18C6 extracted species having a 1:1 stoichiometry without providing any information on the presence of chloride in this species.

Extraction experiments have been performed with various concentrations of Cr(VI) ($[Cr]_{aq} = 0–0.02$ M) diluted in 2 M hydrochloric acid with DC18C6 (abbreviated L) in dichloromethane. The corresponding distribution isotherms $[Cr]_{org}/[L]_0 = f([Cr]_{aq})$ (Fig. 2) for various initial concentrations of DC18C6 ($[L]_0$ = 0.005, 0.01, and 0.02 M) show that the organic phase is saturated for

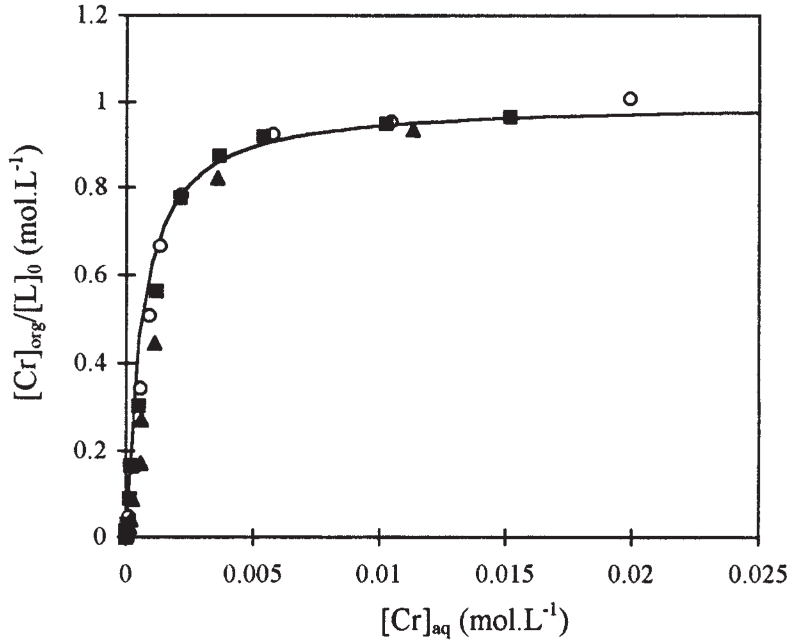

FIG. 2 Isotherm distribution curves $[Cr]_{org}/[L]_0 = f([Cr]_{aq})$ of the extraction of chromic acid from a hydrochloric acid medium with various initial DC18C6 concentrations: (■) 0.005M, (○) 0.01 M, and (▲) 0.02 M. Comparison of the predictive model (solid line) and the experimental results of chromium(VI) extraction using DC18C6.

$[Cr]_{aq} > 0.005$ M and for a $[Cr]_{org}/[L]_0$ ratio close to one, as pointed out by Koshima and Onishi (18).

In order to get more information on the chemical nature of the extracted species, the coextraction of chloride ions and chromium acid was performed. It was shown that in the absence of chromic acid, hydrochloric acid is extracted by DC18C6 in a very low proportion $[Cl^-]/[L]_0 < 0.04$ (Fig. 3) whereas, in the presence of chromic acid (Fig. 4), the organic chloride ion concentration was found to be very close to the organic chromium concentration, showing the existence of the lipophilic chlorochromic anion CrO_3Cl^-.

All the results previously mentioned indicate the formation of the complex ion pair $L(H_3O^+)(CrO_3Cl^-)$ in the organic phase species. Therefore, the overall extraction equilibrium

$$H_3O^+ + CrO_3Cl^-_{aq} + L_{org} \rightleftharpoons L(H_3O^+)CrO_3Cl^- \quad \text{(equilibrium 1)}$$

with the corresponding equilibrium constant K_{ex}, written as

$$K_{ex} = [Cr]_{org}/[H_3O^+][L][Cr]_{aq} \quad (1)$$

with

$$[Cr]_{org} = [L(H_3O^+)CrO_3Cl^-]_{org} \quad (2)$$

and

$$[L] = [L]_0 - [Cr]_{org} \quad (3)$$

is proposed.

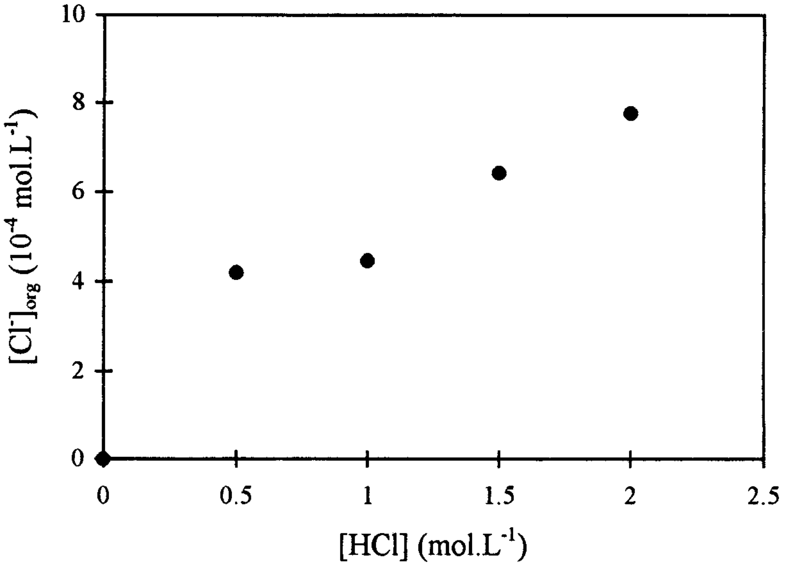

FIG. 3 Isotherm distribution curve of chloride ion extraction without chromium (VI) using DC18C6 ($[L]_0 = 0.02$ M) from hydrochloric acid media with various concentrations.

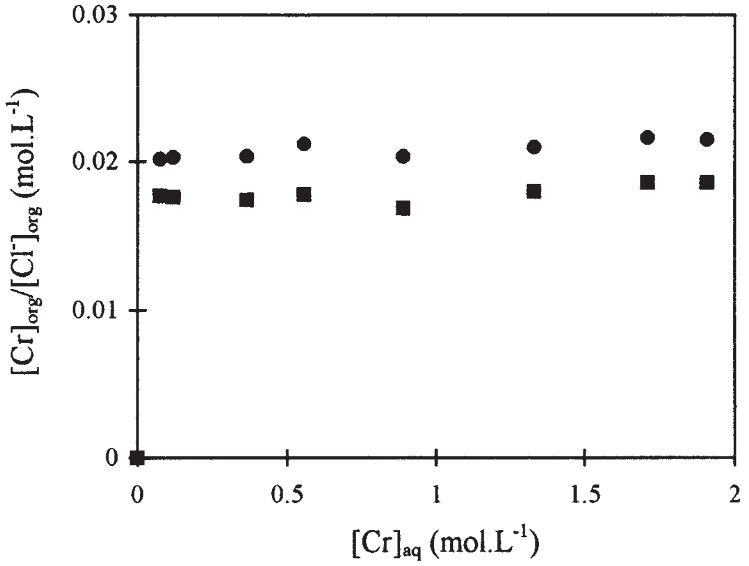

FIG. 4 Isotherm distribution curves of chloride ion (■) and chromium(VI) (●) extraction using DC18C6 ($[L]_0 = 0.02$ M) from a hydrochloric acid medium (2 M).

In the experimental conditions (excess of Cl^-), it is also assumed that

$$[Cr]_{aq} = [CrO_3Cl^-]_{aq} \tag{4}$$

Due to the high acidity of the aqueous extraction medium ($[H_3O^+] \gg [L]_0$), the H_3O^+ aqueous concentration is considered to be constant ($[H_3O^+] = 2$ M) during extraction. Thus, an apparent extraction constant (K_{app}) can be defined as

$$K_{app} = [Cr]_{org}/[L][Cr]_{aq} \tag{5}$$

Using Eqs. (3) and (5), an expression for the chromium(VI) extraction distribution isotherm can be deduced:

$$[Cr]_{org}/[L]_0 = K_{app}\,[Cr]_{aq}/(1 + K_{app}\,[Cr]_{aq}) \tag{6}$$

A satisfactory fit of the experimental $[Cr]_{org}/[L]_0$ versus $[Cr]_{aq}$ plot using Eq. (6) is obtained for $K_{app} = 1700 \pm 100\ mol^{-1}\cdot L$ as shown in Fig. 2 for three initial ligand concentrations (0.005, 0.01, and 0.02 M). It can also be noted that the proposed model is valid for a large range of chromium(VI) concentrations in the aqueous phase ($0 < [Cr]_{aq} < 2\ mol\cdot L^{-1}$).

Stripping of Chlorochromic Acid

Stripping of chlorochromic acid in the organic phase was carried out with pure water (pH ~ 5.5) using various organic chlorochromic acid concentra-

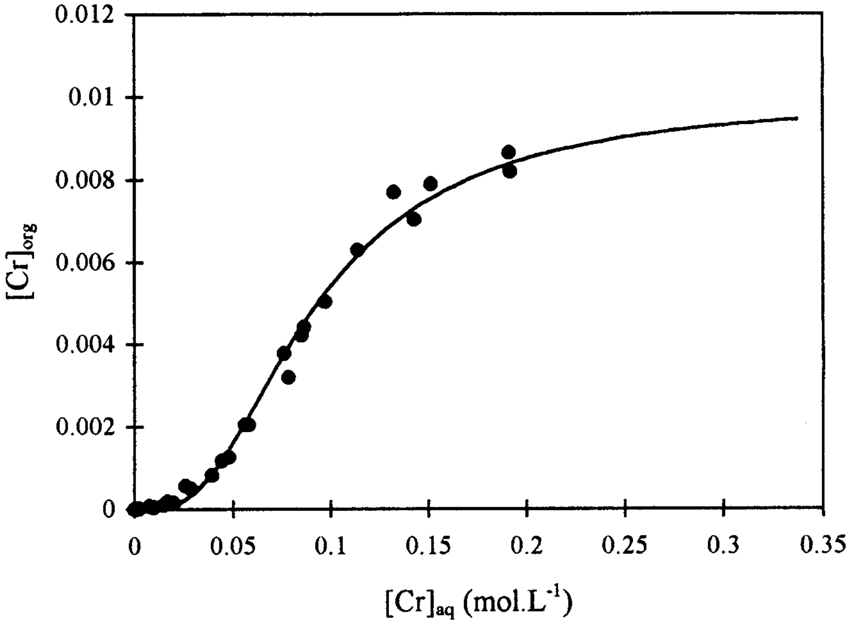

FIG. 5 Comparison of the predictive model (solid line) based on the stripping reaction and the hydrolysis of the CrO_3Cl^- species with the experimental results of the chromium(VI) stripping.

tions, a constant organic/aqueous volume ratio (see Experimental Section), and $[L]_0 = 0.01$ M. The deduced Cr(VI) stripping distribution isotherm (Fig. 5) suggests that chromium saturation of the organic phase is obtained for a 1/1:$[Cr]_{org}/[L]_0$ ratio. This is an additional confirmation of the proposed extracted complex stoichiometry.

The stripping reaction is accompanied in pure water by hydrolysis of the chlorochromate ion (21). Thus, the following equilibria have to be considered:

$$H_3O^+\ LCrO_3Cl^- \rightleftharpoons L + CrO_3Cl^- + H_3O^+ \qquad \text{(equilibrium 2)}$$

$$CrO_3Cl^- + 2H_2O \rightleftharpoons HCrO_4^- + Cl^- + H_3O^+ \qquad \text{(equilibrium 3)}$$

The corresponding equilibrium constants are defined for equilibrium 2 as

$$K_{\text{strip}} = \frac{[L][CrO_3Cl^-][H_3O^+]}{[Cr]_{\text{org}}} \tag{7}$$

and for equilibrium 3 as

$$K_{\text{h}} = \frac{[Cl^-][H_3O^+][HCrO_4^-]}{[CrO_3Cl^-]} \tag{8}$$

where K_h is the CrO_3Cl^- hydrolysis constant (expressed in $mol^2{\cdot}L^{-2}$).

According to equilibria 2 and 3, the concentration of chromium(VI) in the stripping aqueous phase is $[\mathrm{Cr}]_{\mathrm{aq}} = [\mathrm{HCrO^{-}}_4] + [\mathrm{CrO_3Cl^{-}}]$ with $[\mathrm{HCrO_4^{-}}] = [\mathrm{Cl^{-}}]$.

From the electroneutrality of the aqueous stripping phase, it is deduced that

$$[\mathrm{H_3O^+}] = [\mathrm{Cl^-}] + [\mathrm{HCrO_4^-}] + [\mathrm{CrO_3Cl^-}] = [\mathrm{HCrO_4^-}] + [\mathrm{Cr}]_{\mathrm{aq}}$$

The equation of the stripping distribution isotherm is deduced from the previous relations:

$$[\mathrm{Cr}]_{\mathrm{org}} = \frac{\dfrac{1}{K_{\mathrm{strip}}K_{\mathrm{h}}}[\mathrm{L}]_0([\mathrm{HCrO_4^-}] + [\mathrm{Cr}]_{\mathrm{aq}})^2[\mathrm{HCrO_4^-}]^2}{1 + \dfrac{1}{K_{\mathrm{strip}}K_{\mathrm{h}}}([\mathrm{HCrO_4^-}] + [\mathrm{Cr}]_{\mathrm{aq}})^2[\mathrm{HCrO_4^-}]^2} \tag{9}$$

By using Eq. (8), $[\mathrm{Cr}]_{\mathrm{aq}}$ is calculated from $[\mathrm{HCrO_4^{-}}]$ as

$$[\mathrm{Cr}]_{\mathrm{aq}} = \frac{K_{\mathrm{h}}[\mathrm{HCrO_4^-}] + [\mathrm{HCrO_4^-}]^3}{K_{\mathrm{h}} - [\mathrm{HCrO_4^-}]^2} \tag{10}$$

The simulated curve of $[\mathrm{Cr}]_{\mathrm{org}}$ versus $[\mathrm{Cr}]_{\mathrm{aq}}$ using Eq. (10) and the experimental results are reported in Fig. 5. The good agreement with the experimental stripping data, obtained with the stripping constant $K_{\mathrm{strip}} = 6.25 \times 10^{-3}\ \mathrm{mol^2{\cdot}L^{-2}}$ and $K_{\mathrm{h}} = 8.00 \times 10^{-3} \pm 5 \times 10^{-4}\ \mathrm{mol^2{\cdot}L^{-2}}$, supports the validity of the proposed model.

Donnan Equilibrium of the Liquid Membrane

The extraction selectivity of DC18C6 toward chlorochromic acid with respect to hydrochloric acid, associated with the ability of pure water to ensure chromium backextraction (stripping), suggests that the organic phase can work as a semipermeable bulk liquid membrane in a three liquid-phase system. The semipermeability of the liquid membrane is characterized by the Donnan equilibrium isotherm $[\mathrm{Cr}]_{\mathrm{aqII,\ stripping}} = \mathrm{f}([\mathrm{Cr}]_{\mathrm{aqI,\ extraction\ feed}})$, which is deduced from the liquid–liquid extraction and stripping Cr(VI) distribution curves by plotting $[\mathrm{Cr}]_{\mathrm{aqII}}$ versus $[\mathrm{Cr}]_{\mathrm{aqI}}$ for a common $[\mathrm{Cr}]_{\mathrm{org}}$ concentration (Fig. 6).

The $[\mathrm{Cr}]_{\mathrm{aqII}} = \mathrm{f}([\mathrm{Cr}]_{\mathrm{aqI}})$ Donnan equilibrium curve is obtained numerically by considering $\mathrm{HCrO_4^{-}}$ concentration (Eqs. 9 and 10) as a variable from which $[\mathrm{Cr}]_{\mathrm{aqII}}$ and $[\mathrm{Cr}]_{\mathrm{org}}$ are computed. The corresponding $[\mathrm{Cr}]_{\mathrm{aqI}}$ is deduced by means of Eq. (6).

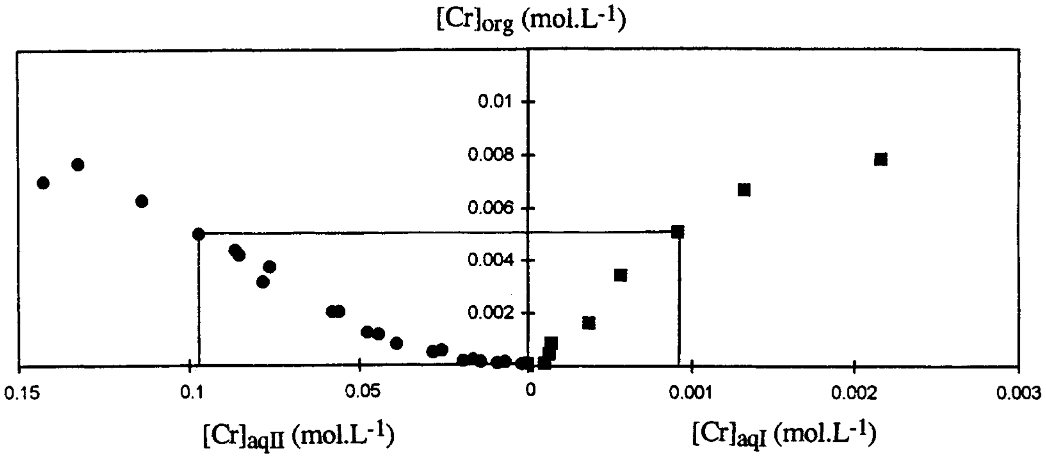

FIG. 6 Liquid–liquid extraction and stripping chromium(VI) distribution curves. Determination of chromium(VI) concentrations in the feed ($[Cr]_{aqI}$) and receiving ($[Cr]_{aqII}$) phase for a common chromium(VI) organic concentration ($[Cr]_{org}$).

The deduced curve (Fig. 7) ($[Cr]_{aqII} = f([Cr]_{aqI})$ predicts the ability of the bulk liquid membrane to concentrate chlorochromic acid in the receiving phase within the experimental conditions (i.e., for an overall HCl concentration in the feed phase). The ability to concentrate chomium can be defined by

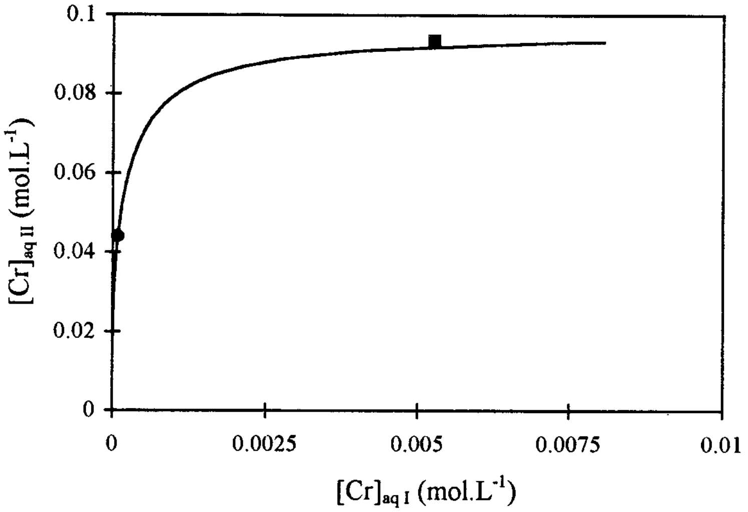

FIG. 7 Donnan equilibrium curve $[Cr]_{aqII,\ stripping} = f([Cr]_{aqI,\ extraction\ feed})$ (solid line) deduced from extraction and stripping equilibria. Chromium equilibrium states obtained from transport experiments after 8 hours: (●) initial chromium(VI) concentration in the feed = 0.05 M, carrier concentration = 0.01 M; (■) initial chromium(VI) concentration in the feed = 0.01 M, carrier concentration = 0.02 M.

the ratio $\alpha = [\mathrm{Cr}]_{\mathrm{aqII}}/[\mathrm{Cr}]_{\mathrm{aqI}}$ which varies in the range $\sim 35 \leq \alpha \leq \sim 280$ for low chromium(VI) concentrations in the feed phase ($0.0002\ \mathrm{M} < [\mathrm{Cr}]_{\mathrm{aqI}} < 0.0025\ \mathrm{M}$).

This result can be generalized to any liquid membrane system containing a highly selective extractant carrier (L) which transports chlorochromic acid from a 2 M HCl feed to a water receiving phase via the formation of a complex of general formula $\mathrm{L(H_3O^+)CrO_3Cl^-}$ in the membrane phase.

Liquid Membrane Transport Experiments

Two different kinetic experiments were carried out to illustrate chromium(VI) transport through the liquid membrane (Figs. 8 and 9). The equilibrium state is reached and characterized by the occurrence of near plateau values for chromium concentrations in the feed, receiving, and liquid membrane phases.

In Experiment I the volume of the two aqueous phases is equal ($V_{\mathrm{aqI}} = V_{\mathrm{aqII}} = 0.05$ L). The initial concentration of chromium(VI) in the feed aqueous phase was 0.05 M in 2 M HCl ($[\mathrm{L}]_0 = 0.01$ M). In this case an almost quantitative transfer of chromium(VI) is obtained with a very high corresponding concentration factor ($\alpha = 513$). In Experiment II ($[\mathrm{Cr}]_0 = 0.01$ M, $[\mathrm{L}]_0 = 0.02$

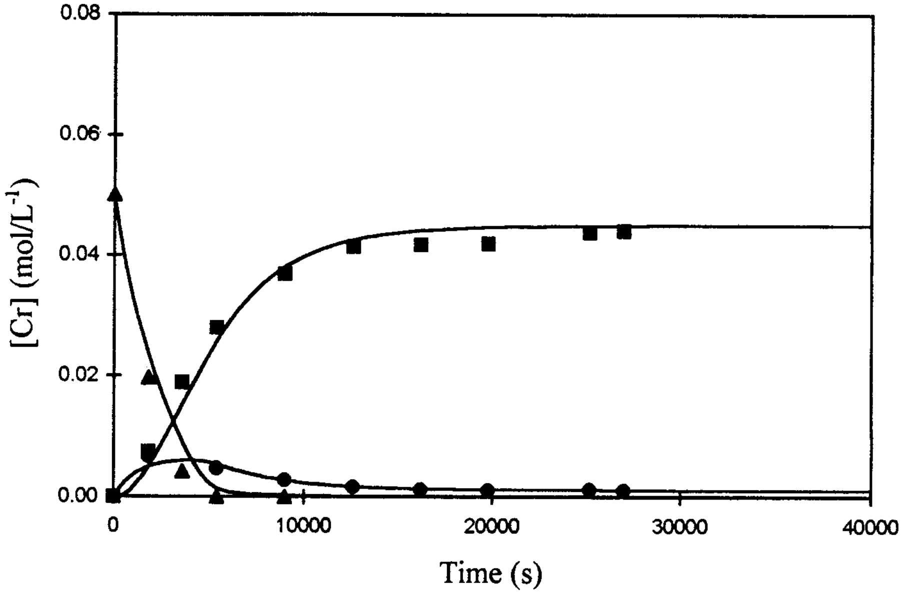

FIG. 8 Evolution of chromium(VI) concentrations during transport through a liquid membrane containing DC18C6 in dichloromethane. Initial concentrations: $[\mathrm{L}]_0 = 0.01$ M and $[\mathrm{Cr}]_0 = 0.05$ M. Chromium(VI) concentration: (■) in the feed phase, (●) in the organic phase, (▲) in the receiving phase. Comparison of the predictive model (solid line) and the experimental results of chromium(VI) transport.

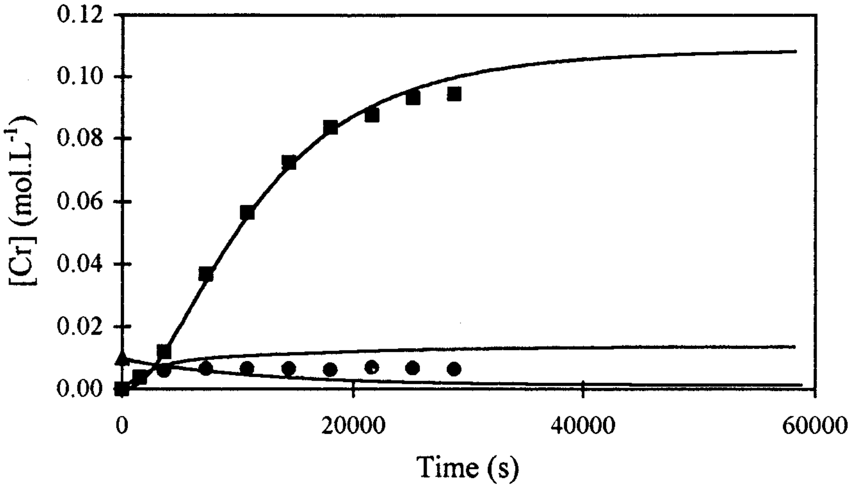

FIG. 9 Evolution of chromium(VI) concentrations during transport through a liquid membrane containing DC18C6 in dichloromethane. Initial concentrations: $[L]_0 = 0.02$ M and $[Cr]_0 = 0.005$ M. Chromium(VI) concentration: (■) in the feed phase, (●) in the organic phase, (▲) in the receiving phase. Comparison of the predictive model (solid line) and the experimental results of chromium(VI) transport.

M), the volume of the two phases is different ($V_{\mathrm{aqI}} = 1$ L, $V_{\mathrm{aqII}} = 0.05$ L). Near plateau concentration values are obtained for an α value which is much lower ($\alpha = 18$) than in Experiment I. It is experimentally confirmed in both cases that the corresponding equilibrium point ($[\mathrm{Cr}]_{\mathrm{aqI}}$ and $[\mathrm{Cr}]_{\mathrm{aqII}}$, reported in Fig. 7) is close to the Donnan equilibrium state, predicted from the extraction and stripping equilibria (Eqs. 6, 9, and 10).

Kinetic Modeling of Chromium(VI) Transport

The modeling of the mass transfer kinetics is carried out by applying the two-film model at each liquid membrane interface (26). In this model the rate-limiting step of the transfer is assumed to be chromium(VI) diffusion through the two stagnant films adjacent to a given interface. The transfer rate is then described by fluxes, deduced from Fick's law, which characterize the diffusion of chromium(VI) through the various stagnant films (19):

$$J_{\mathrm{aq}\,1} = -\frac{V_{\mathrm{aqI}}}{S_1}\, d\,\frac{[\mathrm{Cr}]_{\mathrm{aqI}}}{dt} = k_{\mathrm{aq}\,1}\left([\mathrm{Cr}]_{\mathrm{aqI}} - [\mathrm{Cr}]_{\mathrm{aq\,int}\,1}\right) \tag{11}$$

$$J_{\mathrm{org}\,1} = k_{\mathrm{org}\,1}\left([\mathrm{Cr}]_{\mathrm{org\,int}\,1} - [\mathrm{Cr}]_{\mathrm{org}}\right) \tag{12}$$

$$J_{\mathrm{org}\,2} = k_{\mathrm{org}\,2}\left([\mathrm{Cr}]_{\mathrm{org}} - [\mathrm{Cr}]_{\mathrm{org\,int}\,2}\right) \tag{13}$$

$$J_{\mathrm{aq}\,2} = -\frac{V_{\mathrm{aqII}}}{S_2}\, d\,\frac{[\mathrm{Cr}]_{\mathrm{aqII}}}{dt} = k_{\mathrm{aq}\,2}\left([\mathrm{Cr}]_{\mathrm{aq\,int}\,2} - [\mathrm{Cr}]_{\mathrm{aqII}}\right) \tag{14}$$

with the mass balance equation

$$S_1 J_{\mathrm{aq}\ 1} - S_2 J_{\mathrm{aq}\ 2} = V_{\mathrm{org}} \frac{d[\mathrm{Cr}]_{\mathrm{org}}}{dt} \tag{15}$$

where $[\mathrm{Cr}]_{\mathrm{aq\ int}\ 1}$, $[\mathrm{Cr}]_{\mathrm{org\ int}\ 1}$, $[\mathrm{Cr}]_{\mathrm{aq\ int}\ 2}$, and $[\mathrm{Cr}]_{\mathrm{org\ int}\ 2}$ are the aqueous and organic interfacial concentrations; $k_{\mathrm{aq}\ 1}$, $k_{\mathrm{aq}\ 2}$, $k_{\mathrm{org}\ 1}$, and $k_{\mathrm{org}\ 2}$ are the corresponding mass transfer coefficients; S_1 and S_2 are the interfacial areas; and V_{org} is the membrane phase volume.

Assuming conservative fluxes for each interface:

$$J_{\mathrm{aq}\ 1} = J_{\mathrm{org}\ 1} \tag{16}$$

$$J_{\mathrm{org}\ 2} = J_{\mathrm{aq}\ 2} \tag{17}$$

Concentrations are related by the following overall mass balance equation:

$$V_{\mathrm{aqI}}\,[\mathrm{Cr}]_{\mathrm{aqI}} + V_{\mathrm{aqII}}\,[\mathrm{Cr}]_{\mathrm{aqII}} + V_{\mathrm{org}}\,[\mathrm{Cr}]_{\mathrm{org}} = V_{\mathrm{aqI}}\,[\mathrm{Cr}]_0 \tag{18}$$

with the boundary conditions

$$t = 0,\ [\mathrm{Cr}]_{\mathrm{aqI}} = [\mathrm{Cr}]_0;\ [\mathrm{Cr}]_{\mathrm{org}} = 0;\ [\mathrm{Cr}]_{\mathrm{aqII}} = 0$$

Additional approximations are made here:

$$k_{\mathrm{aq}\ 1} = k_{\mathrm{org}\ 1} = k_1 \tag{19}$$

$$k_{\mathrm{aq}\ 2} = k_{\mathrm{org}\ 2} = k_2 \tag{20}$$

and

$$k_1 = 1.2 k_2 \tag{21}$$

These approximations have been found to be satisfactory for the setup used in this work (27).

Within the two-film model, Eqs. (6) and (9) provide the relations between the interfacial concentrations at the two interfaces, respectively.

Interface 1:

$$[\mathrm{Cr}]_{\mathrm{org\ int}\ 1} = \frac{1700[\mathrm{L}]_0[\mathrm{Cr}]_{\mathrm{aq\ int}\ 1}}{1 + 1700[\mathrm{Cr}]_{\mathrm{aq\ int}\ 1}} \tag{6}$$

Interface 2:

$$[\mathrm{Cr}]_{\mathrm{org\ int}\ 2} = \frac{20{,}000[\mathrm{L}]_0([\mathrm{HCrO}_4^-] + [\mathrm{Cr}]_{\mathrm{aq\ int}\ 2})^2[\mathrm{HCrO}_4^-]^2}{1 + 20{,}000([\mathrm{HCrO}_4^-] + [\mathrm{Cr}]_{\mathrm{aq\ int}\ 2})^2\,[\mathrm{HCrO}_4^-]^2} \tag{9}$$

Because of the complexity of Eq. (9), an empirical equation ($[\mathrm{Cr}]_{\mathrm{org\ int}\ 2} = 58[\mathrm{L}]_0[\mathrm{Cr}]_{\mathrm{aq\ int}\ 2}{}^2$) has been used and found to be valid for the concentration range $0 < [\mathrm{Cr}]_{\mathrm{aq\ int}\ 2} < 0.1\ \mathrm{mol}\cdot\mathrm{L}^{-1}$.

Differential equations are solved by applying the classical Euler method:

$$\frac{d[\mathrm{Cr}]_i}{dt} = \frac{\Delta[\mathrm{Cr}]_i}{\Delta t} = kf([\mathrm{Cr}]_i), \qquad \text{with } i = \mathrm{aqI}, \mathrm{aqII}, \text{ and org}$$

$$V_{\mathrm{org}} \frac{[\mathrm{Cr}]_{i,n+1} - [\mathrm{Cr}]_i}{t_{n+1} - t_n} = kS_i f([\mathrm{Cr}]_i), \qquad \text{with } t_{n+1} - t_n = \tau$$

which provide $[\mathrm{Cr}]_{\mathrm{aqI}}(t)$, $[\mathrm{Cr}]_{\mathrm{aqII}}(t)$, and $[\mathrm{Cr}]_{\mathrm{org}}(t)$ for a given value of k. Calculations were performed for $\tau = 300$ seconds.

Comparison between the experimental and calculated $[\mathrm{Cr}]_i = f(t)$ curves (Fig. 8) shows that the transfer process is described for close values of k ($k_1 = 38.0\ \mu\mathrm{m}\cdot\mathrm{s}^{-1}$ for Experiment I and $k_1 = 36.0\ \mu\mathrm{m}\cdot\mathrm{s}^{-1}$ for Experiment II). These mass transfer coefficients are of the same magnitude as for the transport of chromic acid from sulfate media ($k_1 = 43.0\ \mu\mathrm{m}\cdot\mathrm{s}^{-1}$) (19). This agreement supports the validity of the approach.

CONCLUSION

Dicyclohexano-18-crown-6 appears to be an appropriate extractant carrier for the recovery of chlorochromic acid from a hydrochloric acid medium. Liquid–liquid extraction studies have shown that chromium(VI) is extracted via a complex ion pair $\mathrm{L(H_3O^+)(CrO_3Cl^-)}$.

The presented approach links the extraction and stripping processes with transfer through the liquid membrane by deducing the Donnan equilibrium of the DC18C6-containing membrane from a two-phase distribution equilibria.

Actual transport experiments show the ability to concentrate chromium (“uphill transport”) as predicted by the Donnan equilibrium diagram.

The present study also illustrates the relatively high transfer intensity (high transfer coefficients) combined with a high selectivity which can be obtained by a liquid membrane with respect to a classical membrane.

NOMENCLATURE

[Cr]	chromium VI concentration ($\mathrm{mol\cdot L^{-1}}$)
[L]	extractant carrier concentration ($\mathrm{mol\cdot L^{-1}}$)
S	interface area ($\mathrm{dm^2}$)
V	phase volume (L)
t	time (s)
J	chromium flux ($\mathrm{mol\cdot s^{-1}\cdot dm^{-1}}$)
k	mass transfer coefficient ($\mu\mathrm{m\cdot s^{-1}}$)

Indices

aq	aqueous phase
org	organic phase
I	in the extraction phase or feed aqueous bulk
II	in the receiving phase or stripping aqueous bulk
int	interface
1	interface between the feed phase and the membrane
2	interface between the receiving phase and the membrane
0	initial concentration conditions

REFERENCES

1. B. J. Page and G. W. Loar, in *Encyclopedia of Chemical Technology*, 4th ed, Wiley, New York, NY, 1992, p. 263.
2. K. R. Newby, in *Metal Finishing 59th Guidebook and Directory*, (P. H. Langdon, Ed.), Metals and Plastics Publications, Inc., Hackensack, NJ, 1991, pp. 179.
3. G. M. Ritcey, in *Tailings Management Problems and Solutions in the Mining Industry* (Process Metallurgy 6), Elsevier, New York, NY, p. 500.
4. A. K. Guha, C. H. Yun, R. Basu, and K. K. Sirkar, *AIChE J.*, *40*, 1223 (1994).
5. C. Deptula, *J. Inorg. Nucl. Chem.*, *30*, 1309 (1968).
6. Y.-H. Huang, C.-Y. Chen, and J.-F. Kuo, *Hydrometallurgy*, *28*, 297 (1992).
7. Y.-H. Huang, C.-Y. Chen, and J.-F. Kuo, *Bull. Chem. Soc. Jpn.*, *64*, 3059 (1991).
8. B. G. Fraser, M. D. Pritzker, and R. L. Legge, *Sep. Sci. Technol.*, *29*, 2097 (1994).
9. I. Ortiz, B. Galan, and A. Irabien, *Ind. Eng. Chem. Res.*, *35*, 1369 (1996).
10. E. Salazar, M. I. Ortiz, A. M. Urtiaga, and J. A. Irabien, *Ibid.*, *31*, 1523 (1992).
11. A. I. Alonso, B. Galan, A. Irabien, and I. Ortiz, *Sep. Sci. Technol.*, *32*, 1543 (1997).
12. T. Sato, T. Nakamura and Y. Takeushi, *Solv. Extr. Ion Exch.*, *2*, 1033 (1984).
13. D. G. Tuck and R. M. Walters, *J. Chem. Soc.*, p. 1111 (1963).
14. J. P. Cuer, W. Stuckens, and N. Texier in *Proceedings of the International Solvent Extraction Conference (ISEC '74)*, Society of the Chemical Industry, London, 1974, p. 1185.
15. C. K. Mann and J. C. White, *Anal. Chem.*, *30*, 989 (1958).
16. K. Takahashi, K. Hirayama, and H. Takeushi, *Solv. Extr. Ion Exch.*, *5*, 393 (1987).
17. M. A. Gashgari, A. Al-Yobi, and M. Ejaz, *Sep. Sci. Technol.*, *25*, 903 (1990).
18. H. Koshima and H. Onishi, *Anal. Sci.*, *9*, 141 (1993).
19. A. Zouhri, M. Burgard, and D. Lakkis, *Hydrometallurgy*, *38*, 299 (1995).
20. M. Burgard, L. Jurdy, H. S. Park, and R. Heimburger, *Nouv. J. Chim.*, *7*, 575 (1983).
21. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., Wiley, New York, NY, 1988, p. 679.
22. I. Dellin, F. M. Hall, and L. G. Hepler, *Chem. Rev.*, *76*, 283 (1976).
23. J. Y. Tong and R. L. Johnson, *Inorg. Chem.*, *5*, 1902 (1966).
24. G. P. Haight Jr., D. C. Richardson, and N. H. Colburn, *Ibid.*, *3*, 1777 (1964).
25. N. Miralles, A. Sastre, and M. Aguilar, *Polyhedron*, *6*, 2145 (1987).
26. J. M. Coulson, J. F. Richardson, J. R. Backhurst, and J. H. Harker, *Chemical Engineering, Vol. II*, 4th ed., Pergamon, Oxford, 1991, p. 597.
27. T. Delloye, M. Burgard, and M. J. F. Leroy, *New J. Chem.*, *13*, 139 (1989).

Received by editor May 15, 1998
Revision received September 1998

PAGE 1906 IS BLANK

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Downloaded At: 11:09 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at
http://www.dekker.com/servlet/product/DOI/101081SS100100745