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

Permeation of Chromium(VI) and Rhenium(VII) Oxyanions through Liquid Organic Membranes Facilitated by Quaternary Ammonium Chlorides

Jerzy Strzelbicki[a]; Witold A. Charewicz[a]; Alina Mackiewicz[a]
[a] INSTITUTE OF INORGANIC CHEMISTRY AND METALLURGY OF RARE ELEMENTS TECHNICAL UNIVERSITY OF WROCLAW, WROCAW, POLAND

To cite this Article Strzelbicki, Jerzy , Charewicz, Witold A. and Mackiewicz, Alina(1984) 'Permeation of Chromium(VI) and Rhenium(VII) Oxyanions through Liquid Organic Membranes Facilitated by Quaternary Ammonium Chlorides', Separation Science and Technology, 19: 4, 321 — 336

To link to this Article: DOI: 10.1080/01496398408068586

URL: http://dx.doi.org/10.1080/01496398408068586

SEPARATION SCIENCE AND TECHNOLOGY, 19(4&5), pp. 321-336, 1984

Permeation of Chromium(VI) and Rhenium(VII) Oxyanions through Liquid Organic Membranes Facilitated by Quaternary Ammonium Chlorides

JERZY STRZELBICKI, WITOLD A. CHAREWICZ, and ALINA MACKIEWICZ

INSTITUTE OF INORGANIC CHEMISTRY AND METALLURGY OF RARE ELEMENTS
TECHNICAL UNIVERSITY OF WROCLAW
50-370 WROCAW, POLAND

Abstract

An experimental investigation is presented on the facilitated transport of Cr(VI) and Re(VII) oxyanions from aqueous solution into and through organic solutions of quaternary ammonium chlorides as mobile carriers of anions. Trimethyl tallow ammonium chloride (Aliquat 26), dimethyl dicoco ammonium chloride (Aliquat 221), and methyl tricapryl ammonium chloride (Aliquat 336) from General Mills Chemicals have been investigated. Effects of both anions and mobile carriers as well as the pH of feed aqueous solution and mixing rate on the course of metal permeation have been established. The hydrophobicity and nucleophilicity of a quaternary ammonium chloride were found to be the key factors influencing the transport of Cr(VI) and Re(VII) anions through bulk and emulsified liquid organic membranes. The permeation of perrhenates was much faster than that of chromates. Fast and effective separation was determined to be possible for rhenium from chromium in aqueous solution by means of facilitated transport of their oxyanions across liquid surfactant membranes.

INTRODUCTION

Up-to-date investigations on liquid membrane separation of inorganic ionic species from aqueous solutions have been essentially limited to metal cations. Only a few works (*1–3*) have been reported involving separation of anionic species. Since many metals of subgroups V, VI, and VII form stable anions,

0149-6395/84/1904-0321$3.50/0

the recognition of facilitated transport of such species through liquid organic membranes could contribute to the practical potential of this novel separation technique.

We herewith report on an experimental investigation of the permeation of chromium(VI) and rhenium(VII) oxyanions across both bulk and emulsified liquid organic membranes facilitated by quaternary ammonium chlorides as mobile carriers as well as on the liquid–liquid extraction of these anions from aqueous solution into kerosene solutions of quaternary ammonium chlorides. The study involves quaternary ammonium chlorides of varying molecular structure in order to estimate the possible effects of the physicochemical properties of both anions and mobile carriers on the course of permeation.

EXPERIMENTAL SECTION

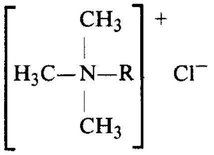
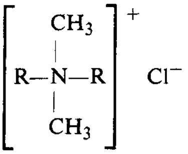
Apparatus

Concentration of chromates and perrhenates was determined radiometrically using radioisotopes ^{186}Re and ^{51}Cr and multichannel gamma radiation spectrometer ND-1200 (Nuclear Data Co.) with a semiconductor probe (Ge/Li). Measurements of the pH of aqueous solutions were made with pH meter N-517 (Mera-Elwro) using a glass body combination electrode SAg P-209 W (Energopomiar). Constant pH levels of feed aqueous solution were maintained during membrane permeation experiments with our own constructed pH controller to control a peristaltic pump S-31 (Domet).

Reagents

Quaternary ammonium chlorides Aliquat 26, Aliquat 221, and Aliquat 336 were from General Mills Chemicals (Table 1). Sorbitan monooleate (Span 80) was from Loba Chemie (Austria) while polybutadiene (average molecular weight from 6000 to 6500) was from the Institute of Plastic and Organic Technology, Technical University of Wrocław (Poland). Polish commercial kerosene ($d = 0.876$) was used as the organic solution. Radioisotopes ^{186}Re and ^{51}Cr were from Centre of Production and Distribution of Radioisotopes, Swierk (Poland). The source of the other chemicals (all of them reagent grade) was POCh (Poland). Double distilled water was used as the solvent for inorganic reagents.

TABLE 1
Quaternary Ammonium Chlorides Used as Mobile Carriers for Re(VII) and Cr(VI) Oxyanions (*4*)

Chemical name, trade name, and abbreviation	Chemical formula	Molecular weight
Trimethyl tallow ammonium chloride, Aliquat 26, A26	 $\left[H_3C-\overset{CH_3}{\underset{CH_3}{N}}-R\right]^+ Cl^-$ R = 3% C_{14}, 25% C_{16}, 25% C_{18} saturated; 3% C_{16}, 44% C_{18} unsaturated	337
Dimethyl dicoco ammonium chloride, Aliquat 221, A221	 $\left[R-\overset{CH_3}{\underset{CH_3}{N}}-R\right]^+ Cl^-$ R = 1% C_8, 5% C_{10}, 55% C_{12}, 22% C_{14}, 10% C_{16}, 3% C_{18} saturated; 4% C_{18} unsaturated	449.5
Methyl tricaprylyl ammonium chloride, Aliquat 336, A336	$[CH_3NR_3]^+ Cl^-$ $R = (CH_2)_6CH_3$	404.2

Procedure

Liquid–Liquid Extraction

The kerosene solution (10 mL) of a quaternary ammonium chloride and the aqueous solution (10 mL) of NH_4ReO_4 or K_2CrO_4, NaCl (to maintain constant ionic strength), and NaOH or NCl (to control pH), with adequate radioisotope (as perrhenate or chromate), was shaken mechanically at ambient temperature (19 ± 1°C) for 20 and 15 min when Cr(VI) on Re(VII) oxyanions were extracted, respectively. Thereafter the phases were separated, the equilibrium pH of the aqueous phase was measured, and 1 mL samples of both organic and aqueous phases were removed for radioactivity measurements.

Bulk Liquid Membrane Permeation

Bulk liquid membrane permeation was conducted with a beaker-in-beaker type cell (Fig. 1) where the organic phase (75 mL) was a solution of quaternary ammonium chloride (mobile carrier) in toluene. The source phase (200 mL) was the aqueous solution of NH_4ReO_4 or K_2CrO_4 with adequate radioisotope. The acidity of the source phase containing potassium chromate was kept at a constant level by adding aqueous hydrochloric acid. The receiving phase (25 mL) was aqueous sodium hydroxide (3.0 mol/L) for chromate transport and ammonium rhodanate (2.0 mol/L) for perrhenate transport. The source/organic and organic/receiving phases interfacial areas were equal to 7.55 and 25.3 cm^2, respectively. Each of the three phases was stirred separately at stirring rates ranging from 100 to 150 rpm, and the samples of each phase were periodically removed during each experiment to measure their radioactivity and then returned to the system.

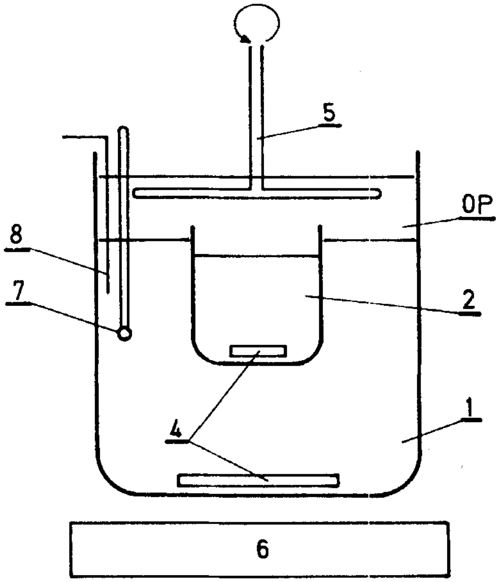


FIG. 1. Bulk liquid membrane transport cell: (1) aqueous feed solution, (2) aqueous receiving phase, (OP) organic phase (bulk membrane), (4) magnetic bars, (5) glass stirrer, (6) magnetic stirrer, (7) combination electrode, (8) glass tube for adding HCl solution.

Emulsified Liquid Membrane Permeation

Water-in-oil type emulsions were made by stirring at 1300 rpm for 40 min in a xylene solution (10 mL) of quaternary ammonium chloride (mobile carrier), Span 80 (emulsifier), and (in some cases) polybutadiene (viscosity regulator) with an aqueous receiving solution (10 mL) of stripping reagent ($NaOH$ or NH_4SCN) at ambient temperature (19 ± 1°C). The resultant emulsion was then mixed with an aqueous feed solution (100 mL) of NH_4ReO_4 or K_2CrO_4 labeled with adequate radioisotope. The pH of the feed solution containing K_2CrO_4 was kept at a constant level by adding aqueous hydrochloric acid. Samples of this solution were removed periodically during a transport experiment for determination of radioactivity. Then the emulsion was separated from the external feed solution and broken by adding 1–2 mL of *n*-butanol. The radioactivities of the resultant organic and receiving phases were measured.

RESULTS AND DISCUSSION

Liquid–Liquid Extraction

Results on the extraction of chromium(VI) oxyanions from the aqueous solution at an initial metal concentration of 0.05 mol/L into 0.2 mol/L kerosene solution of quaternary ammonium chloride are summarized in Figs. 2 and 3. With quaternary ammonium chlorides A221 and A336, the extractability of Cr(VI) oxyanions was only slightly dependent on the equilibrium pH which ranged from 1 to 6. A26 exhibits a somewhat different extraction capability for Cr(VI) oxyanions since the fraction of chromium extracted (5) decreases when the equilibrium pH ranges from 1 to 3. This fraction remains constant when the pH ranges from 3 to 6. With all three quaternary ammonium chlorides, chromium(VI) extraction fell when the equilibrium pH exceeded 6. Extractive efficiencies evaluated from the data in Fig. 2 for examined quaternary ammonium chlorides toward chromates follow the order A336 > A221 > A26. In terms of both the molecular structure of quaternary ammonium chloride and the ionic equilibrium in aqueous solution of Cr(VI) oxyanions, an increasing number of hydrocarbon chains makes the molecule of a quaternary ammonium chloride larger and thus more hydrophobic, which results in an improvement of its extractive efficiency toward monovalent anions (*6–8*). Second, under our experimental conditions, CrO_4^{2-} anions prevail in basic and slightly acidic aqueous

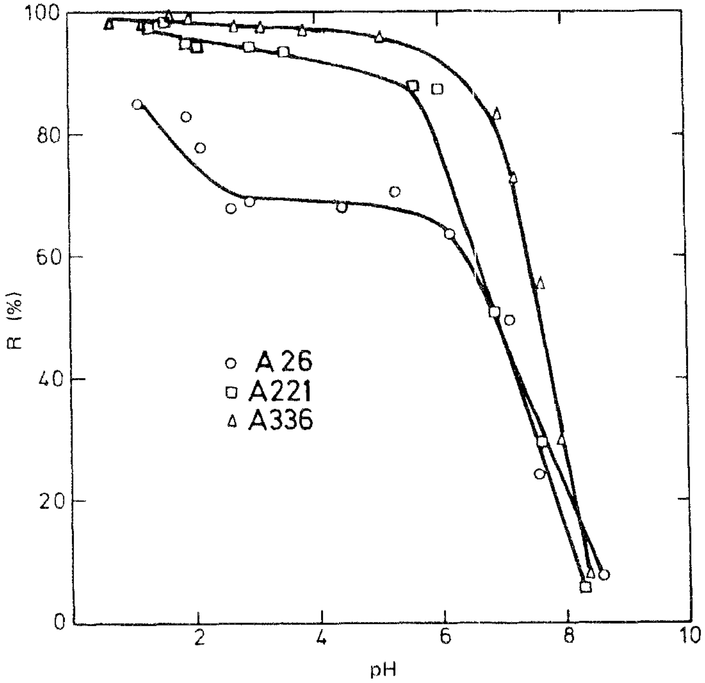


FIG. 2. Fraction extracted (*R*, %) of Cr(VI) with various quaternary ammonium chlorides vs equilibrium pH of aqueous phase.

solution, and $Cr_2O_7^{2-}$ anions dominate in acidic aqueous Cr(VI) solution. Moreover, $Cr_2O_7^{2-}$ anions convert into $HCrO_4^-$ anions in acidic aqueous solution at a total chromium(VI) concentration lower than (1.26–1.74) × 10^{-2} mol/L (*9*). It has been found (*10, 11*) that quaternary ammonium salts exhibit reasonable extraction abilities only toward monovalent Cr(VI) oxyanions; i.e., $HCrO_4^-$ and $HCr_2O_7^-$. Therefore, both a decrease of the Cr(VI) fraction extracted (Fig. 2) and inflections in the Cr(VI) distribution coefficients (Fig. 3) at an equilibrium pH exceeding 6.0 are reasonable in terms of conversion of $HCrO_4^-$ into $Cr_2O_7^{2-}$ or CrO_4^{2-} (*9*).

Results on the extraction of perrhenates from aqueous solution of initial concentration 0.1 mol/L into 0.05 mol/L kerosene solution of a quaternary ammonium chloride are summarized in Table 2. The slight influence of equilibrium pH on the fraction of Re(VII) extracted has been observed only for Aliquat 26. That strong extractability of perrhenate anions with quaternary ammonium salts is due to the high affinity of perrhenates toward

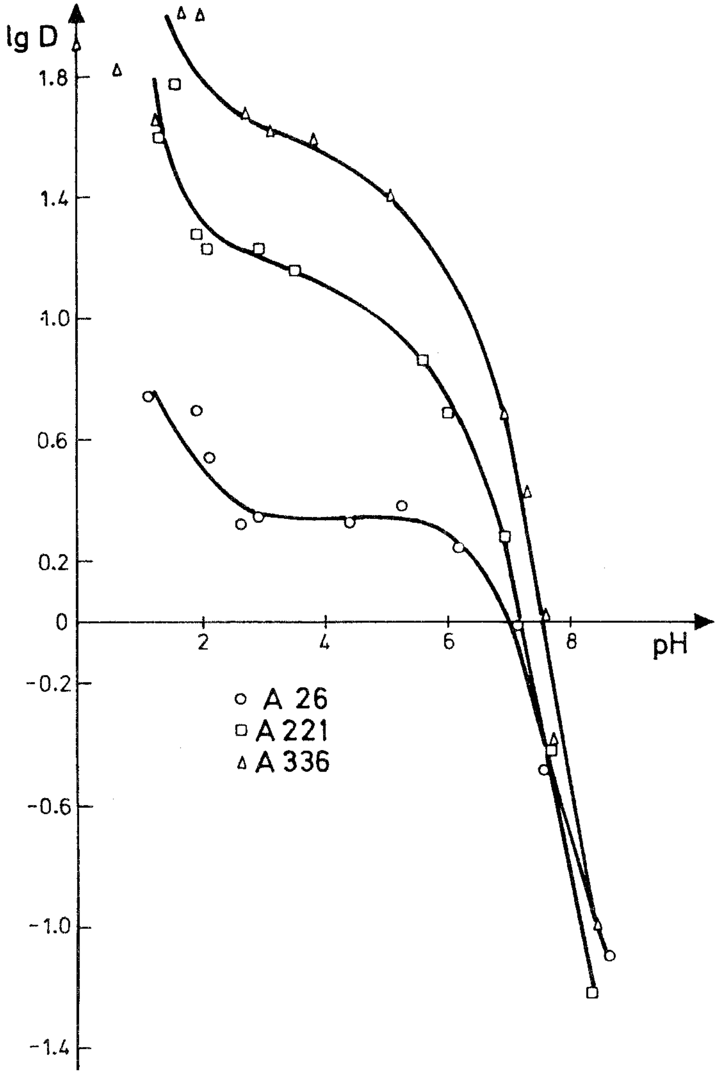


FIG. 3. Distribution coefficient (D) of Cr(VI) with various quaternary ammonium chlorides vs equilibrium pH of aqueous phase.

TABLE 2
Extraction of Perrhenates by Quaternary Ammonium Chlorides

A26		A221		A336	
pH	R (%)	pH	R (%)	pH	R (%)
0.82	84.4	0.98	95.4	1.82	100
0.88	82.6	2.86	95.3	4.35	100
1.2	79.5	3.2	96.5	5.02	100
1.7	79.5	4.1	95.0	8.30	100
2.3	77.3	5.0	97.4		
3.2	73.8	7.0	96.5		
6.3	69.4	7.7	93.8		
8.5	65.5	8.8	94.8		
9.3	80.5	11.8	94.7		
10.2	75.0				
11.6	80.7				

quaternary ammonium cations (*12, 13*). Moreover, it precludes aqueous alkali hydroxides as a stripping medium. Consequently, aqueous NH_4SCN was used for that purpose in both extraction and membrane permeation studies due to the high affinity of SCN^- anions toward quaternary ammonium cations (*12, 13*).

Permeation across Bulk Liquid Membranes

Data from permeation across a bulk liquid membrane are presented in Figs. 4 and 5 as plots of metal concentration in all three phases involved vs time of permeation. The permeation of Cr(VI) and Re(VII) oxyanions has been examined at initial metal concentrations in the aqueous feed solution equal to 1.25×10^{-3} and 2.5×10^{-3} mol/L for chromium and rhenium, respectively. The concentration of quaternary ammonium chlorides in the toluene phase was equal to 6.0×10^{-3} mol/L. The receiving phase was 3 mol/L of sodium hydroxide for chromates and 2 mol/L ammonium rhodanate for perrhenates.

Transport of chromium(VI) oxyanions across a toluene membrane has been investigated at constant pH of the aqueous feed phase equal to 3.5 (where $HCrO_4^-$ anions dominate in the solution under experimental conditions (*9*)) as well as at pH equal to 7.05, 7.10, and 7.65 (where CrO_4^{2-} anions dominate in the feed solution (*9*)) for membranes containing A22, A221, and A336, respectively. These three pH values have been determined

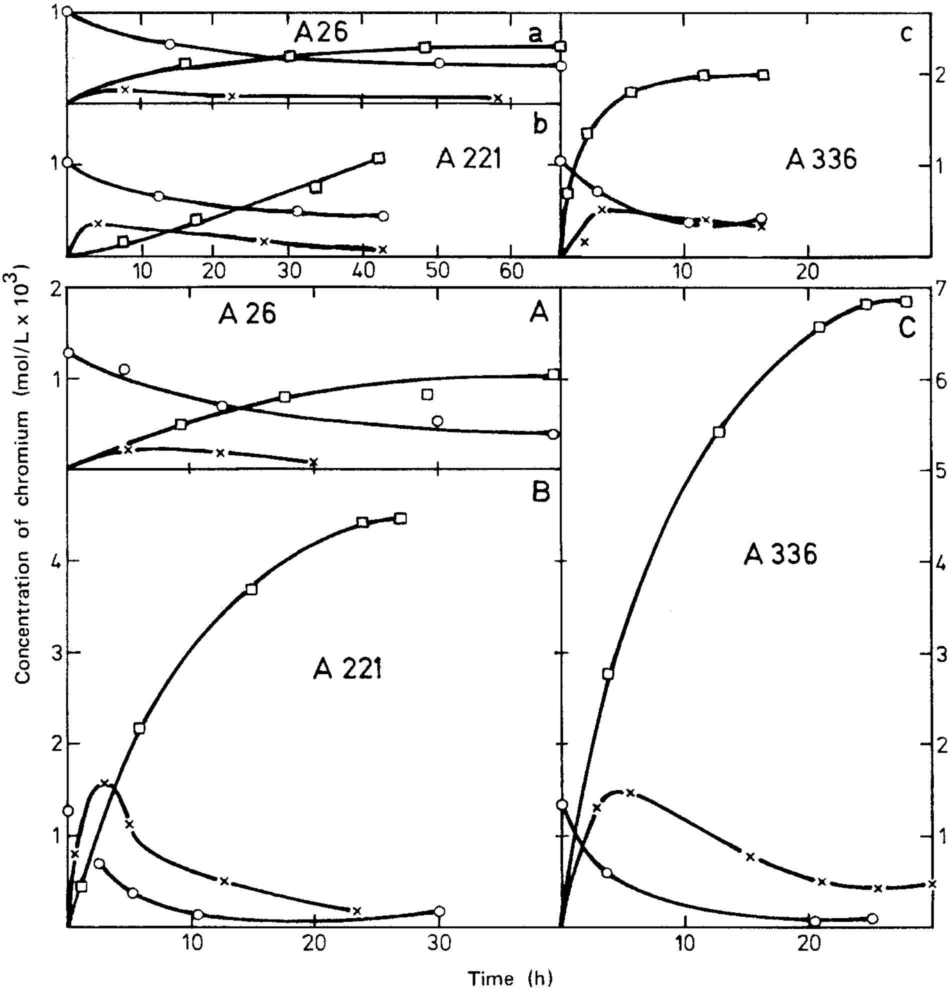


FIG. 4. Kinetics of Cr(VI) transport through bulk liquid membranes containing various quaternary ammonium chlorides at various pH values of the aqueous source phase: (○) source phase, (×) organic phase, (□) receiving phase. pH of the source phase for a, b, and c equal to 7.05, 7.10, and 7.65, respectively; for A, B, and C equal to 3.5.

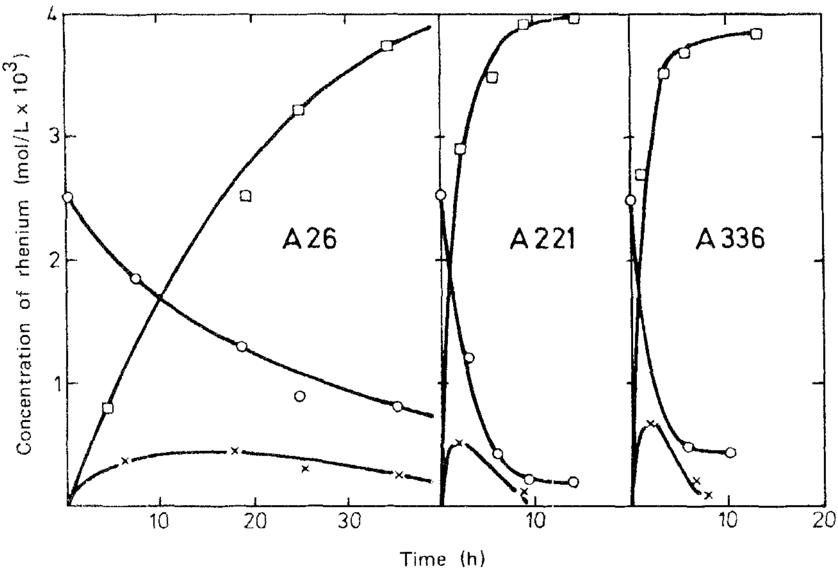


FIG. 5. Kinetics of Re(VII) transport through bulk liquid membranes containing various quaternary ammonium chlorides: (○) source phase, (×) organic phase, (☐) receiving phase.

as $pH_{0.5}$ of chromium(VI) extraction with the quaternary ammonium chlorides examined (Figs. 2 and 3).

From bulk liquid membrane transport experiments it is found that transport of Cr(VI) oxyanions through a toluene solution of quaternary ammonium chlorides is strongly dependent on the acidity of the aqueous source phase while a remarkably enhanced permeation of Cr(VI) anions is observed from acidic media compared to neutral and slightly basic media with all three extractants used. This effect is particularly evident for A221 (Figs. 4B and 4b) and A336 (Figs. 4C and 4c) and can be discussed in terms of the rates of chemical reactions involving a quaternary ammonium chloride and a Cr(VI) oxyanion. The assumption seems reasonable that complexation of monovalent $HCrO_4^-$ anions, which are dominant in acidic aqueous solution, by quaternary ammonium cations is much faster than complexation of chromium(VI) oxyanions in neutral and basic aqueous solution where bivalent CrO_4^{2-} anions prevail. Moreover, the molecular structure of quaternary ammonium salt influences its feasibility as a mobile carrier for anions since an increasing number of hydrocarbon chains and thus of the hydrophobicity leads to an improvement of Cr(VI) oxyanions permeation.

Consequently, the rate of perrhenate permeation was lowest with A26 and increases with A221 and with A336, while the final concentrations of rhenium in the receiving phase were similar (Fig. 5).

Increasing hydrophobicity and nucleophilicity of a quaternary ammonium chloride may also lead to an increase of both the quaternary ammonium cation–inorganic counter anion complex stability and its solubility in an organic solvent. It can be postulated that formation of this complex is the permeation rate-controlling stage since relatively low concentrations of metal anions in the organic phase have been observed at all experimental conditions. Thus, permeation of metal anions across a membrane has not been delayed at the organic/receiving phases interface (almost all metal transported from the source phase into the organic phase passed quickly into the receiving phase). The possibility of the delay of mass transport at the source/organic phases interface has been discussed (*14, 15*).

The somewhat higher metal concentration in the organic phase observed at the beginning of permeation may indicate a sort of "induction" step for a metal stripping reaction at the organic/receiving phases interface. On the other hand, the enhanced permeation of chromates and perrhenates observed with quaternary ammonium chlorides of higher hydrophobicity leads to the conclusion that possible diffusive hindrances of permeation process were negligible under our experimental conditions. Otherwise, more hydrophobic and larger quaternary ammonium molecules should be less effective as mobile carriers for anions.

Permeation across Emulsified (liquid surfactant) Membranes

The results on permeation of Cr(VI) and Re(VII) oxyanions across emulsified (liquid surfactant) membranes are shown in Figs. 6 and 7 for perrhenates and in Fig. 8 for chromates as plots of metal concentration in aqueous feed solution vs time of mixing. The initial concentrations of both rhenium and chromium in the feed solution were 0.005 mol/L while the continuous organic phase of the emulsion was a xylene solution of emulsifier (Span 80) and a quaternary ammonium chloride. Concentrations of organic phase components were: Span 80, 2.0 vol%; quaternary ammonium chloride, 0.01 mol/L; and polybutadiene, 10 vol% for chromates permeation; and Span 80, 0.25 vol%; quaternary ammonium chloride, 0.005 mol/L for perrhenates permeation. The receiving aqueous phase (dispersed phase of the emulsion) was 3.0 mol/L aqueous sodium hydroxide and 2.0 mol/L aqueous ammonium rhodanate for chromate and perrhenate permeation,

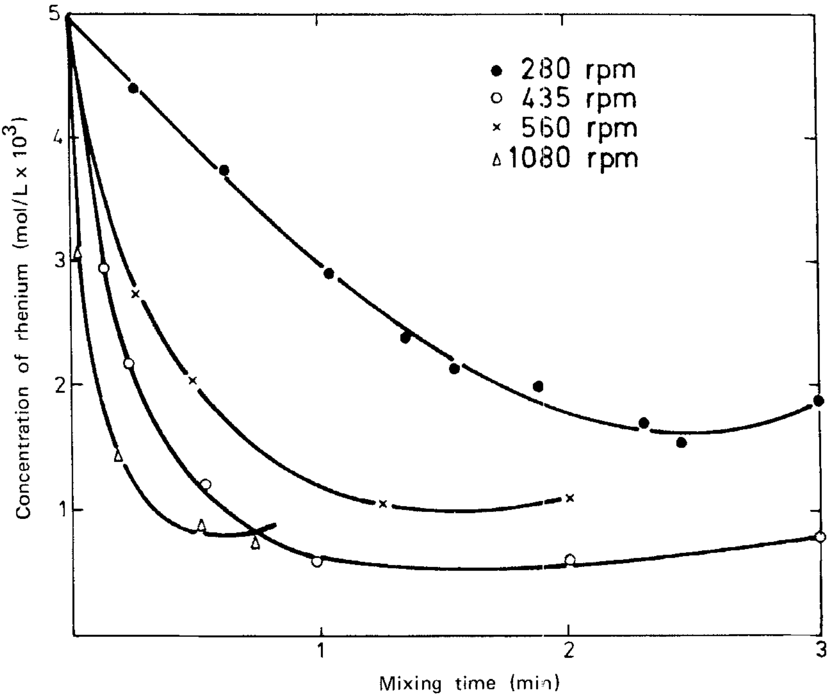


FIG. 6. Concentration of Re(VII) in the external (feed) solution of emulsified (liquid surfactant) membrane containing Aliquat 221 vs time of permeation at various mixing rates.

respectively. The emulsion was mixed with the feed solution at 560 rpm for chromates permeation and at 435 rpm for perrhenates permeation. Additional experiments were conducted on the effect of mixing rate (ranging from 280 to 1080 rpm) on the permeation of perrhenates through an emulsified membrane containing A221 (Fig. 6). It has been determined that mixing rates ranging from 435 to 1080 rpm had no significant influence on the permeation of perrhenates under our experimental conditions.

The data in Figs. 7 and 8 indicates that the molecular structure of the mobile carrier strongly influences the transport of both perrhenates and chromates across emulsified (liquid surfactant) membranes. The rate of this transport increases with the number of hydrocarbon chains in the quaternary ammonium chloride molecule. On the other hand, the fraction of metal transported with A26 was much lower than with A221 and A336. These results are consistent with bulk liquid membrane permeation data where increasing hydrophobicity and nucleophilicity of a quaternary ammonium chloride led to enhancement of transport of Re(VII) and Cr(VI) oxyanions. Thus, these two factors were assumed to govern the transport of oxyanions rather than possible diffusional transport hindrances. With the same mobile carrier, the transport of perrhenates across an emulsified (liquid surfactant) membrane (Fig. 7) was much faster than the transport rate of chromates (Fig. 8). Similarly, saturation of the receiving phase with perrhenates in bulk liquid membrane permeation experiments has been achieved faster than with chromates (Figs. 4 and 5). Such behavior indicates the importance of the physicochemical properties of permeating ions in establishing their permeation across a liquid organic membrane.

The rate of Re(VII) and Cr(VI) oxyanions transport across emulsified (liquid surfactant) membranes was estimated as about two orders higher than the rate of permeation of these anions across a bulk liquid membrane. This illustrates the advantage of emulsified liquid membrane systems because of their large interfacial areas.

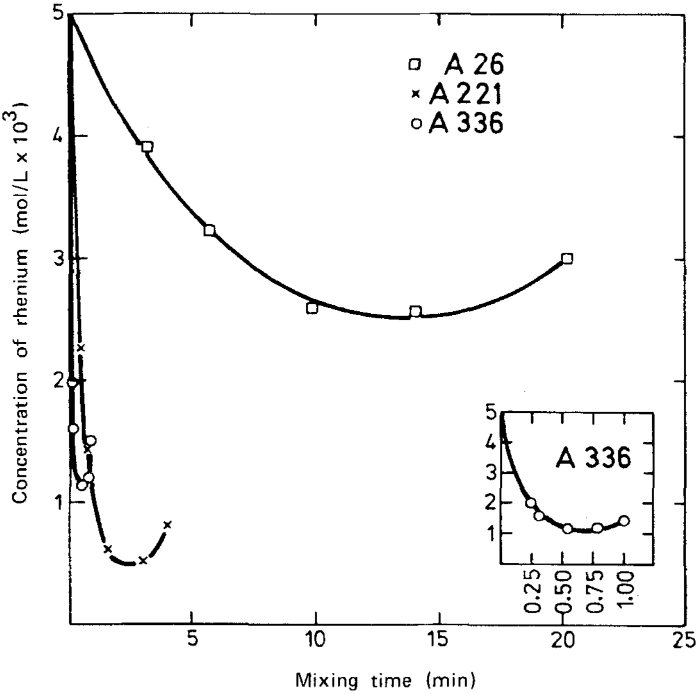


FIG. 7. Concentration of Re(VII) in the external (feed) solution of emulsified (liquid surfactant) membranes containing various quaternary ammonium chlorides vs time of permeation.

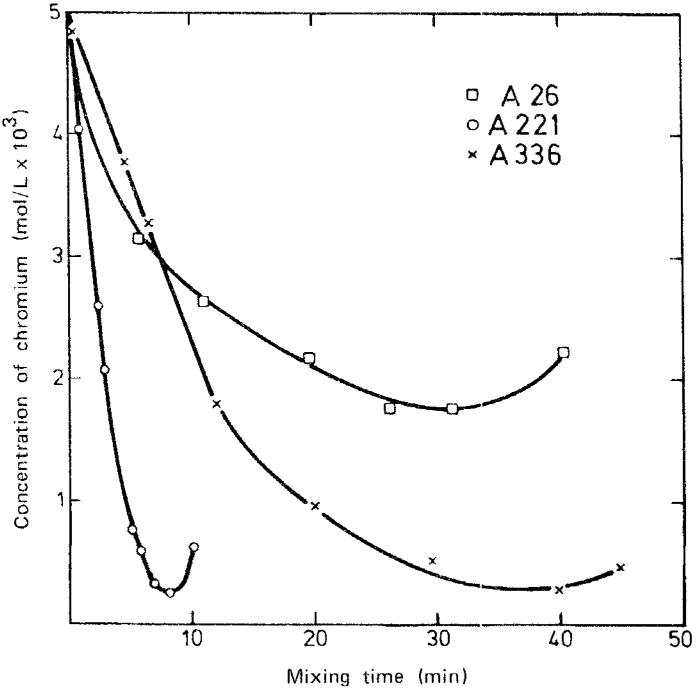


FIG. 8. Concentration of Cr(VI) in the external (feed) solution of emulsified (liquid surfactant) membranes containing various quaternary ammonium chlorides vs time of permeation at constant pH of the feed solution equal to 3.5.

CONCLUSIONS

The facilitated transport of Cr(VI) and Re(VII) oxyanions from aqueous solutions into and through organic solutions of quaternary ammonium chlorides as mobile carriers of anions was determined as governed by the affinity of the carrier toward the transported anion. Quaternary ammonium chlorides containing more hydrocarbon chains in their molecule, and thus being more hydrophobic and nucleophilic, were more effective carriers for the oxyanions studied.

Perrhenates with a stronger affinity for the quaternary ammonium chlorides than the chromates were much better extracted into the organic phase within the pH range examined, and their transport across liquid membranes was faster and more efficient.

The application of two liquid membrane experimental systems (bulk and emulsified) was used in an attempt to explain the mechanism of Re(VII) and

Cr(VI) oxyanions permeation. The bulk liquid membrane system favored convective diffusional mass transport rather than the steady-state diffusional transport. It has been suggested that the transport of Re(VII) and Cr(VI) oxyanions across a bulk liquid membrane is similar in nature to that across an emulsified liquid membrane, and that both are similarly dependent on the affinities of the transported anions toward the quaternary ammonium carriers. This similarity leads to the supposition that convective diffusional mass transport plays an important role (*14*) in the permeation of Re(VII) and Cr(VI) oxyanions across the emulsified liquid membrane. This is reinforced by an observed increase in the Re(VII) and Cr(VI) transport efficiency with mobile carriers of increasing molecular size; i.e., steady-state diffusional mass transport would lead to a reverse dependence.

Under our experimental conditions the rate of the oxyanion complexation reaction seems to control the overall rate of permeation of Re(VII) and Cr(VI) oxyanions across a liquid membrane.

The rate of Re(VII) and Cr(VI) oxyanions transport with quaternary ammonium chlorides across emulsified liquid membranes is estimated to be about two orders higher than their rate of permeation across bulk liquid membranes. This indicates the potential of emulsified (liquid surfactant) membrane systems as a practical separation technique.

Acknowledgment

We would like to thank General Mills Chemicals, Inc., for providing the Aliquat 26, Aliquat 221, and Aliquat 336 used in our experiments.

REFERENCES

1. D. K. Shiffer, A. Hochhauser, D. F. Evans, and E. L. Cussler, *Nature, 250*, 484 (1974).
2. A. M. Hochhauser and E. L. Cussler, *AIChE Symp. Ser., 71*, 136 (1976).
3. T. Kitagawa, Y. Nishikawa, J. W. Frankenfeld, and N. N. Li, *Environ. Sci. Technol., 11*, 602 (1977).
4. *General Mills Fatty Nitrogen Chemicals for Industry*, Technical Bulletin 12-A-3, General Mills Chemicals, Inc.
5. N. M. Rice, *Hydrometallurgy, 7*, 177 (1981).
6. L. M. Gindin and S. N. Ivanova, *J. Inorg. Chem.* (*Russ.*), *10*, 502 (1965).
7. A. K. Babko and A. S. Lozovik, *Ibid., 14*, 1618 (1969).
8. W. S. Shmidt and E. A. Miezhov, *Usp. Khim., 4*, 1388 (1965).
9. C. F. Baes and R. E. Mesmer, *The Hydrolysis of Cations*, Wiley-Interscience, New York, 1976.
10. W. J. Maeck, M. E. Kussy, and G. L. Bockamn, *Anal. Chem., 33*, 1775 (1961).

11. W. J. Maeck, M. E. Kussy, and I. E. Rein, *Ibid., 34*, 1602 (1962).

12. B. Tremillon, *Jonity w procesach rozdzielczych,* PWN, Warsaw, 1970.

13. W. Charewicz and J. Strzelbicki, *J. Chem. Technol. Biotechnol., 29*, 149 (1979).

14. J. Strzelbicki and W. Charewicz, *Hydrometallurgy, 5,* 243 (1980).

15. P. R. Danesi, G. F. Vandegrift, and R. Chiarizia, *Sep. Sci. Technol., 16*(2), 201 (1981).

Received by editor September 23, 1983