This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

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

Kinetics of Formation and Transport Resistances of Zirconium-Monobutyl Phosphate Films

R. W. Freeman[a]; B. Marcos[a]; J. Dillon[a]; H. Demetropoulos[a]
[a] Department of Chemical and Biochemical Engineering Rutgers, The State University of New Jersey, Piscataway, New Jersey

To cite this Article Freeman, R. W. , Marcos, B. , Dillon, J. and Demetropoulos, H.(1987) 'Kinetics of Formation and Transport Resistances of Zirconium-Monobutyl Phosphate Films', Separation Science and Technology, 22: 2, 791 — 800

To link to this Article: DOI: 10.1080/01496398708068981

URL: http://dx.doi.org/10.1080/01496398708068981

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, 22(2&3), 791-800, 1987

Kinetics of Formation and Transport Resistances of Zirconium-Monobutyl Phosphate Films

R. W. FREEMAN, B. MARCOS, J. DILLON, and H. DEMETROPOULOS

DEPARTMENT OF CHEMICAL AND BIOCHEMICAL ENGINEERING
RUTGERS – THE STATE UNIVERSITY OF NEW JERSEY
BOX 909
PISCATAWAY, NEW JERSEY 08854

ABSTRACT

The formation processes of monobutyl phosphate-zirconium films at a liquid-liquid interface have been investigated by observing changes in toluene absorption in a Lewis cell type contactor. Films were formed by adding monobutyl phosphate to the upper (organic) phase and allowing it to react with zirconium dissolved in the lower (aqueous) phase while monitoring the absorption of the organic solvent into the aqueous phase. Results indicate that the film formation occurs over a short period of time but may be preceded by a considerable lag period which depends on concentration, temperature and to a lesser extent, stirring. Mass transfer coefficients were decreased by as much as 40% at higher temperatures. Interfacial tension changes during film formation were also investigated and indicate that significant activity occurs at the interface.

INTRODUCTION

Interfacial films and interfacially located impurities represent one of the major operational problems in liquid-liquid extractions. This material, termed crud, sludge, rag, etc., can drastically alter the performance of solvent extraction equipment. The exact nature of this problem is specific to each operation but involves the accumulation of material at the interface between two liquid phases with a resultant loss in mass transfer efficiency and phase separation performance. Nuclear fuel processing and reprocessing operations are areas where the problem has been particularly troublesome (1-3). The difficulty in cleaning equipment and the restrictions on avoiding criticality make interfacial "crud" particularly unwelcome. This is also one area where specific interfacial films have been identified (4). The reaction between the radiolysis products of tributyl phosphate, the di- and monobutyl phosphates, with zirconium is known to produce interfacial films. This study focuses on the monobutyl phosphate (MBP) in order to avoid the possibility of mixed film content.

The objective of this paper is to develop the experimental technique for analyzing the formation of interfacial films and to demonstrate the method for an important system. Previous work in this specific area is best summarized by Yagodin *et al.* (4) who advanced the hypothesis that these films provide a structural mechanical barrier which retards mass transfer by depressing convection near the surface. His work investigated condensed interfacial films from extraction systems involving zirconium, hafnium and titanium using a Lewis cell contactor. The reported results indicate that mass transfer rates decrease early in the extraction process and that mass transfer coefficients decrease with higher metal concentrations. The work described here extends the investigation to include the kinetics of formation of the films by observing the time required for the film to fully retard the mass transfer process. Information on the concentration and temperature dependence of the film formation process should aid in understanding the fundamental processes involved and provide some direction for reducing the impact of this problem. Understanding the way films reduce mass transfer can help in designing extraction equipment and in modeling the performance of extraction in the presence of these films.

The experimental technique developed for the study of the film formation process is an extension of the method described by Yagodin (4). The approach involves monitoring a parallel extraction and interpreting changes in that extraction as being caused by the interfacial film. The film formation and reaction and concurrent extraction was carried out in a Lewis cell type contactor. This type of contactor has the lighter liquid layered over the heavier liquid. Both phases are stirred but not so vigorously as to disperse one phase into the other. The film formation reaction was conducted by adding MBP to the organic phase and allowing it to react with zirconium dissolved in the aqueous phase while at the same time monitoring the extraction of the organic solvent, toluene, into the aqueous phase. At high concentrations the film formation could be observed visually. At the lower concentrations employed in the analytical study, the film formation could be followed by its effect on the rate of toluene absorption. Toluene was chosen as the solvent/indicating extractant due to its ease of analysis in water by spectrophotometric methods.

THEORY

Mass Transfer in the Lewis Cell

The Lewis cell contactor is appropriate for the study of interfacial films in that it provides a easily measured and homogeneous interfacial region for the formation of the film. Additionally, this contactor is sensitive to the mechanical properties of the film. A rigid film will affect the transfer of turbulence from one phase to the other and thus affect the mass transfer coefficient. Unfortunately, the mass transfer in this situation is very complicated and is not well characterized in that the effect of stirring speed or the presence of interfacial films has not been effectively analyzed. A study (5) using the same cell as the present work indicates that the models originally developed by Lewis (6,7) are as valid as any of the more recent models (8,9).

Although the detailed modeling of the mass transfer processes in a Lewis cell are difficult, the analysis required to obtain values of the mass transfer coefficient is straightforward, particularly when one of the phases is a pure component and thus contributes no resistance to mass transfer. For a constant mass transfer coefficient, the flux (N) in mol/sq cm/min is given by

$$N = k(C^{*} - C^{b}) \qquad [1]$$

were C^{*} is the solubility of toluene in water, C^{b} is the concentration of toluene in the aqueous phase and k is the mass transfer coefficient. With this expression for the flux, a material balance on the system yields

$$\ln\left[\frac{C^{*} - C^{b}}{C^{*} - C^{bo}}\right] = \frac{-S\,k\,t}{V} \qquad [2]$$

where C^{bo} is the bulk concentration at zero time, S is the surface area for mass transfer and V is the volume of the aqueous phase. Equation [2] is used to obtain the mass transfer coefficient from the observed change in concentration with time as a plot of the left hand side of the equation versus time has a slope of -Sk/V.

Mass Transfer with Interfacial Films

Surface films can affect the interphase mass transfer in two ways: by providing a diffusional barrier at the interface or by affecting the convective transport near the interface. The diffusional barrier can be modeled as a series resistance so that

$$1/k = 1/k' + 1/k'' \qquad [3]$$

where k is the overall mass transfer coefficient, k' is the diffusional mass transfer coefficient in the aqueous phase and k'' the mass transfer coefficient across the interfacial film.

If the surface film has mechanical properties that affect the movement of the interface, then the turbulent transfer modeling mentioned above (6 - 9) would have to be modified and k' as well as k'' would be a function of the film properties. Essentially the interaction of the stirring in the two phases would be modified by the existence of the film.

EXPERIMENTAL

Apparatus

The contactor used in these experiments is a modified Lewis cell based on the design of Landau and Chin (10). Figure 1 is a diagram of the apparatus. The cell is cylindrical and divided into two regions each supplied with its own stirring device. The lighter phase is contained in the upper portion and contacts the lower denser fluid at the annular interface. The stirrers are housed in a perforated shell located axially with respect to the cylinder. The shell extends into both compartments but contains a solid partition to prevent contact of the two phases except at the annular space between the shell and the cylinder. The bottom impeller is operated by a shaft extending upward through the shell support rod.

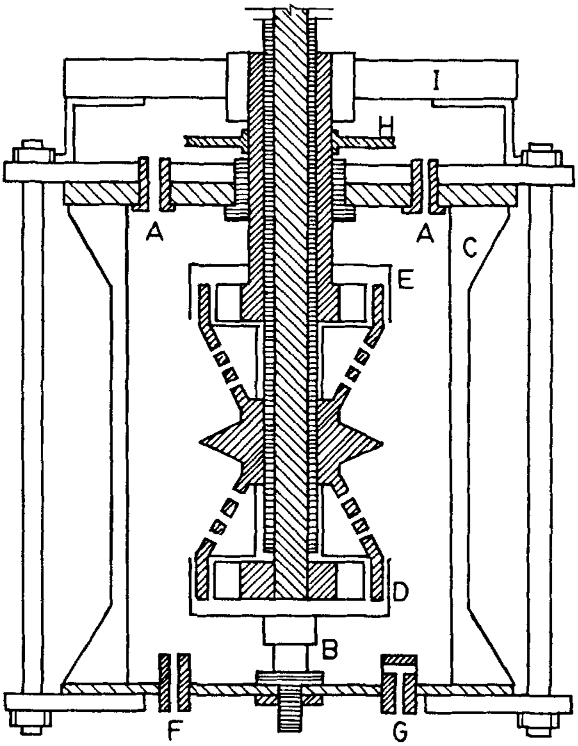

Figure 1. Detail of the Lewis cell contactor: A - fill port; B - bottom support; C - glass cylinder; D,E - end caps; F - outlet port; G - inlet port; H - lower pulley; I - bearing support.

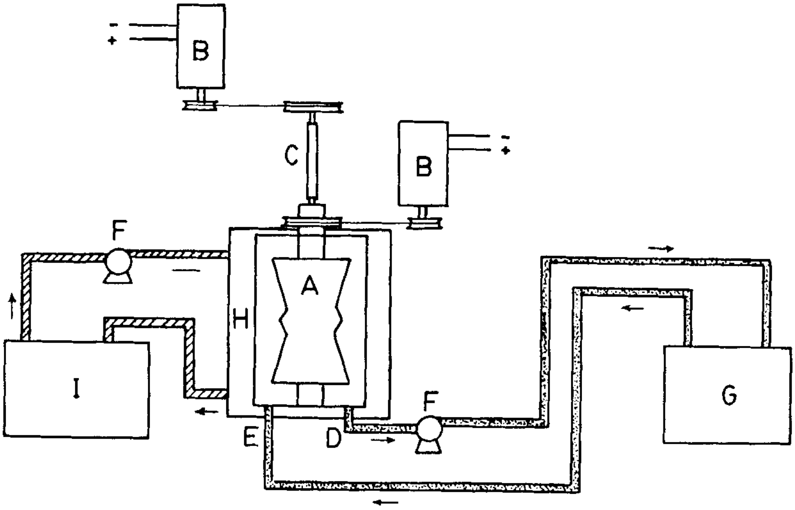

Figure 2. Schematic of the Experiment: A - Lewis cell; B - motor; C - flexible coupling; D - outlet port; E - inlet port; F - pump; G - spectrophotometer ; H - water jacket; I - constant temperature bath.

The upper impeller is operated by a shaft surrounding the shell support rod. Both impellers are of the turbine type. The shell is equipped with caps to prevent transfer of vorticity to the bulk liquid. The fluid flows into the shell through holes in the caps and is forced outward through the perforations in the shell wall. The outer cylinder is a 13.5 cm O.D. glass cylinder, 15 cm in height. The impellers are 1.5 cm in height with a diameter of 5 cm. The shell is 6.5 cm in diameter and 10 cm in height. The impellers are driven by two independently controlled motors and rotate in opposite directions. All surfaces in the cell are Teflon or glass.

Figure 2 is a schematic of the experiment. Connections at the bottom of the cell allow a portion of the fluid in the lower chamber to be circulated continuously through a UV spectrophotometer (G) in order to monitor the bulk phase composition. The cell is equipped with a water jacket (H) to control the temperature.

The interfacial tension measurements were taken with a Fisher Surface Tensiomat Model 21 using the deNouy ring method.

Procedure

Toluene-water experiments were conducted by filling the lower half of the cell with a known volume of water and then layering a known volume of toluene on the top. The stirrers were adjusted to the desired speed and the toluene concentration in the aqueous phase monitored at 260 nm. For the experiments involving zirconium phosphate films the aqueous phase was an acidified zirconium sulfate oxide solution and the organic phase was toluene with 1 ml of MBP added after the stirring rates were adjusted. The MBP was separated from a commercially available mixture of mono- and dibutyl phosphates by the method of Hardy and Scargill (11).

RESULTS AND DISCUSSION

The presence and formation of interfacial films has been observed through the effect of these films on transfer of toluene into water. Changes in the rate of absorption of toluene when film forming material is present is attributed to the effect of these films on the hydrodynamics in the interfacial region or to the creation of an interfacial barrier to mass transfer. Changes in the interfacial tension are attributed to the adsorption of material at the interface and to film formation.

Mass Transfer Measurements

Three types of results have been observed in the the mass transfer experiments: in some experiments the mass transfer was unaffected by the presence of film forming material; in other experiments, there was a reduction in the mass transfer coefficient over essentially the entire experiment; in some experiments the rate of mass transfer changed abruptly at some time during the experiment. Figure 3 is an example of the third type of experimental results. The rate of extraction during the first portion of the experiment illustrated in Figure 3 is essentially identical to the rate observed when no film forming material was added. The rate during the second portion is typical of the rate observed in those experiments where a film is assumed present. These observations can be interpreted as indicating that the film formation occurs suddenly after an initial lag period. This lag period is observed to vary with reactant concentrations, temperature and stirring of the aqueous and organic phases. Tables 1 and 2 provide details of the observed results.

Effect of MBP on transfer. The addition of MBP to the system does not appear to change the mass transfer rates substantially (see entries five through eight of Table 2). The fifth entry in Table 1 however shows anomalous results. Doubling of the MBP concentration produced a large increase in the no-film mass transfer rate. A possible explanation is that the additional MBP promoted interfacial turbulence, thus increasing the mass transfer rate. As will be discussed later, the interfacial tension of these systems is complex and exhibits the type of behavior which could lead to surface instabilities.

Effect of stirring. Stirring has an effect on the film formation time, the mass transfer rate in the absence of a film and the mass transfer rate with a film present. It appears that increased organic phase stirring increases the time required for the film to form. This could be due to increased agitation near the interface on the organic side retarding the formation of a cohesive film. Increased organic phase stirring also seems to increase the no-film mass transfer rates. Since the organic phase is pure, no transfer resistance exists on the organic

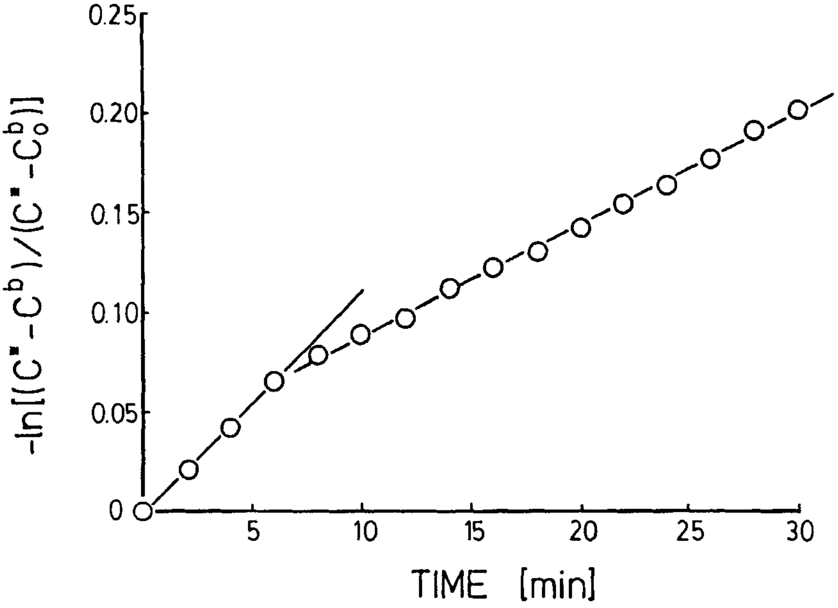

Figure 3. Two regimes of toluene transfer in the presence of MBP and zirconium salt. Experimental conditions: stirring, 415 rpm upper, 450 rpm lower; 0.02% MBP; 2.4 x10^{-6} M zirconium; temperature, 40 °C.

side. Any increase in the no-film mass transfer rate must result from increased turbulence transfer into the aqueous phase. An alternate possibility is that the increased stirring caused increased transport of MBP to the interface which destabilized the interface. The observed increase in film mass transfer rates by organic phase stirring is more difficult to explain, but might be connected with the increased film formation time. A less ordered film structure formed under higher agitation rates might provide less resistance to mass transfer.

Reduced aqueous phase stirring results in longer film formation times and in reductions in the mass transfer when films and no films are present. Increased aqueous phase stirring appears to have little effect on the mass transfer (see the last entry in Table 2). This implies that the power input no longer influences the mass transfer process.

Effect of zirconium concentration. The primary effect of different zirconium levels is on the film formation time. As the concentration increases, the time required to form a film decreases. This is to be expected as the zirconium is a reactant in the film formation process.

Effect of temperature. The effect of temperature on the film formation time is substantial as is to be expected if the film is formed

TABLE 1
Experiments Exhibiting Two Regimes of Mass Transfer

Stirring (rpm) (org/aqu)	Temp. (^oC)	MBP (Vol %)	Zr (M) $\times 10^6$	kl* (cm/min)	k2* (cm/min)	Formation** Time (min)
415/450	40	0.02	2.4	0.0728	0.0393	2
415/250	40	.02	9.4	.0685	.0251	2
550/450	40	.02	9.4	.0946	.0475	4
415/450	25	0.02	18.5	.096	0.077	6
415/450	25	.04	9.4	.175	.068	7
550/450	25	.02	9.4	.172	.135	13

* kl and k2 are the mass transfer coefficients for the first and second regimes respectively.

** Estimated from change in absorption rates.

TABLE 2
Experiments Exhibiting a Single Regime of Mass Transfer*

Stirring (rpm) (org/aqu)	Temp. (^oC)	Zr (M) $\times 10^6$	k (cm/min)	Regime
415/450	40	0**	0.062	no film
415/450	40	9.4	.041	film
415/450	40	9.4	.046	"
415/450	40	4.7	.047	"
415/450	25	0**	0.080	no film
415/450	25	9.4	.071	"
415/450	25	4.7	.079	"
415/450	25	2.4	.065	"
415/250	25	9.4	0.050	no film
415/600	25	9.4	0.069	"

* MBP concentration 0.02 volume % except where noted.

** No MBP in system.

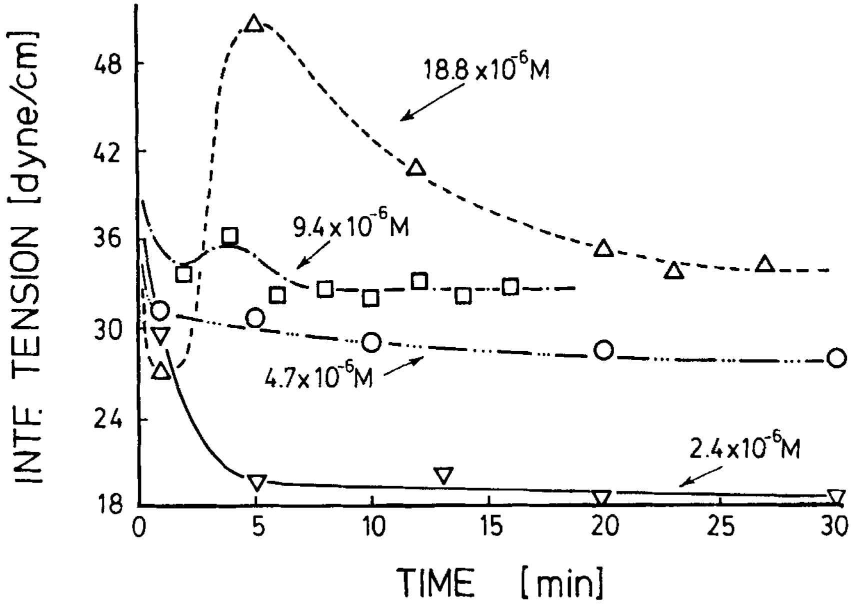

Figure 4. Variation of Interfacial Tension with Time. The concentration of MBP is 0.02 volume %.

by a chemical reaction. The third and sixth entries in Table 1 illustrate this: increasing the temperature from 25 to 40°C decreases the formation time from 13 to 4 minutes. The effect is also evident in that films are observed at lower zirconium concentrations at the higher temperatures.

The effect of temperature on the mass transfer is more complicated. In the absence of MBP, increasing the temperature decreases the mass transfer coefficient as can be seen by entries one and five in Table 2. This effect is due to the complex interactions of the temperature dependencies of the diffusion coefficients, kinematic viscosities and interfacial tension. Additions of MBP do not appear to change this trend.

Interfacial Tension

The interfacial tension of the toluene/water/MBP-Zr system has been measured for four different zirconium concentrations over the time period when film formation was thought to occur. The experimental conditions were chosen to correspond to the mass transfer experiments but without stirring. The results are presented in Figure 4. For the two lower zirconium levels, the decrease in interfacial tension is monotonic with the lowest concentration exhibiting a lower interfacial tension. This could be caused by two competing processes: lowering of the interfacial tension by uncomplexed MBP acting as a surface active agent and the increase in interfacial tension caused by a cohesive film being formed. At the lower zirconium level the first phenomenon is more evident. Raising the zirconium concentration reduces the amount of MBP available, thus increasing the interfacial tension.

The results for the two higher zirconium concentrations exhibit not only this trend of increasing interfacial tension with increasing zirconium concentrations but other changes as well. There appears to be an initial drop followed by an increase in interfacial tension and then a decline to a steady state value. The initial drop could be caused by MBP adsorption. Formation of a structured, cohesive film could then increase the measured interfacial tension. The slow decline might indicate a gradual degradation of the film's structure to some steady state value.

CONCLUSIONS

The experimental observations can be interpreted by postulating the formation of a zirconium-monbutyl phosphate film at the interface between the two solvents. This film is observed to retard mass transfer in significant amounts and could be important in the design and engineering of solvent extraction systems using these components. Film formation, as evidenced by the decrease in mass transfer, appears to occur rapidly after a lag time which depends on a variety of factors including the zirconium concentration, the MBP concentration, the stirring in both phases and the temperature. The experimental approach of using a coextraction process to monitor the presence and condition of surface films appears to be successful and should prove to be a useful tool in such systems.

REFERENCES

1. Ritcey, G. M., Wong, E. W., ISEC 83, 88, (1983).
2. Crouse, D. J., Arnold, W. D. and Hurst, F. J., ISEC 83, 90, (1983).
3. Garrat, D. G., ISEC 83, 94, (1983).
4. Yagodin, G. A., Tarasov, V. V., Fomin, A. V. and Ivakhno, S. Y., ISEC 77, 260, (1977).
5. Demetropoulos, H. and Freeman, R. W., "Barrier Effects of Interfacial Resistances in Liquid-Liquid Systems," presented at AIChE Nat. Meeting, Philadelphia, Aug., 1984.
6. Lewis, J. B., Chem. Eng. Sci., 3, 248 (1954).
7. Lewis, J. B., Chem. Eng. Sci., 3, 260 (1954).
8. Bulicka, J., Prochazka, J., Chem. Eng. Sci., 31, 137 (1976).
9. Bulicka, J., Prochazka, J., Coll. Czech. Chem. Comm., 41, 3180 (1976).
10. Landau, J., Chin, M., Can. J. Chem. Eng., 55, 161 (1977).
11. Hardy, C. J., Scargill, D., J. Inorg. Nucl. Chem., 10, 323 (1959).