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RC-11 Transient Behaviour of Interacting Extractive System

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ABSTRACT

The aim of this study is to investigate the dynamic behaviour of mixer-settler extractive system, which represents an interacting one. When a stimulus single is introduced to aqueous feed; the response of the aqueous phase of the first stage is considered as stimulus signals to both organic phase in the same stage and the aqueous phase of the second one. The response of the last phase represents-in turn-stimulus signals to both organic phase in the same stage and the aqueous phase in the next one. Mathematical model was derived for a system consisting of two stages in the cascade. The model assumed a continuous stirred tank reactor (CSTR) for mixer zone and variable holdups and flow rates of both aqueous and organic phases during operation. Non-linear equilibrium relation was considered. The obtained model - being non-linear- was linearized and Laplace transformation method was used to solve the model. The system constants are those corresponding to extraction of uranyl nitrate from 3N nitric acid solution using TBP dissolved in kerosene at 30% of the former. Stimulus-response test was carried out on the model by considering a step increase in solute concentration in aqueous feed stream. The system behaviour was tested at different values of operating parameters. First order behaviour for the first stage was observed and higher order for the rest of the system. A general relation for the difference in the power of the denominator and numerator of the transfer function of the  $i^{\text{th}}$  stage was concluded for aqueous phase. The study showed that the system overdamps over the practical range of chosen parameters as explained from the values of transfer function roots.

*Key Words: Stimulus-response / Extraction / Interacting system / transient behaviour / Uranyl nitrate.*

INTRODUCTION

The multadvantages of mixer-settler as an extractive system explain the large number of studies which manipulate its behaviour. The majority of these studies had assumed linear relation of equilibrium concentration of solute in the aqueous and organic phases<sup>(1-12)</sup>. Neglecting the effect of variation of flow rate on the system dynamics was also dominant<sup>(8-12)</sup>. This is because of the probability of flooding during operation. In spite of that, few articles had investigated the hydrodynamics of mixer-settler<sup>(12,13)</sup>.

In the present work, the model was derived by assuming non-linear equilibrium relation given by Homg<sup>(14)</sup>. Laplace transformation was used to solve the model when a step signal in solute concentration of aqueous feed is considered.

## MODEL DERIVATION

The model was derived with the help of a set of assumptions. The most important of them is the nonlinearity of equilibrium relation. In addition, lumped parameter system was assumed for the mixer zone and reaction mechanism was that suggested by Moore (15). The details of these assumption are given elsewhere (13). Figure (1) represents two stages mixer-settler, the model equations are expressed for component mass balance, the solute to be

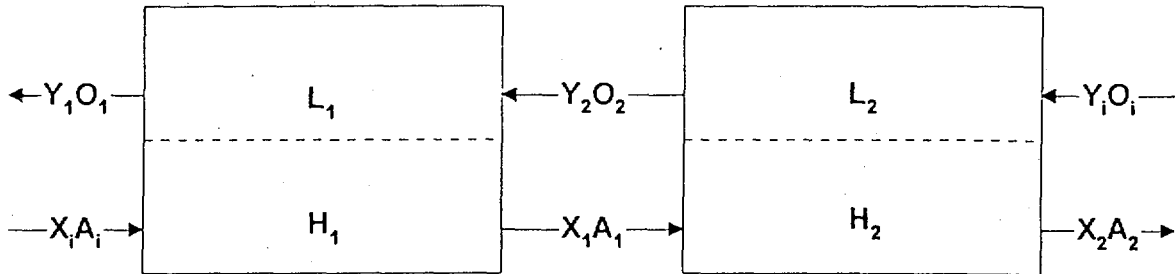


Fig. (1): Schematic representation of two stages mixer-settler

### 1- First Stage Aqueous Phase

$$\frac{d(H_1 X_1)}{dt} = A_i X_i - A_1 X_1 - k_{h1} H_1 (X_1 - X_1^*) \quad (1)$$

### 2- Organic Phase in the First Stage

$$\frac{d(L_1 Y_1)}{dt} = O_2 Y_2 - O_1 Y_1 + k_{l1} L_1 (X_1 - X_1^*) \quad (2)$$

### 3- Aqueous Phase in Second Stage

$$\frac{d(X_2 H_2)}{dt} = A_1 X_1 - A_2 X_2 - k_{h2} H_2 (X_2 - X_2^*) \quad (3)$$

### 4- organic phase in second stage

$$\frac{d(L_2 Y_2)}{dt} = O_i Y_i - O_2 Y_2 + k_{l2} L_2 (X_2 - X_2^*) \quad (4)$$

### 5- Equilibrium Relation

$$Y^* = \frac{B.C.X^*}{1 + C.X^*} \quad (5)$$

where:

$H, L$  : aqueous and organic phase holdups, respectively

$A, O$  : respective aqueous and organic phase flowrates

$X, Y$  : aqueous and organic phase concentration, respectively

$k_h, k_l$  : respective mass transfer coefficient depending on aqueous and organic phase.

$B$  and  $C$  : constants of equilibrium relation depend upon normality of nitric acid, concentration of TBP in solvent and operating temperature.

Equations (1) - (4) are non-linear. By linearization subtracting the corresponding steady state equations and Laplace transformation of the deviation equations produced, the following equations were obtained:

$$X_1(s) = \frac{1}{s + 1/\tau_1} \left[ \frac{1}{\tau_{a1}} X_i(s) + k_h X_1^*(s) \right] \quad (6)$$

$$Y_1(s) = \frac{1}{s + 1/\tau_{o1}} \left[ \frac{1}{\tau_{a2}} Y_2(s) + k_l X_1(s) - k_l X_1^*(s) \right] \quad (7)$$

$$X_2(s) = \frac{1}{s + 1/\tau_2} \left[ \frac{1}{\tau_{a2}} X_1(s) + k_h X_2^*(s) \right] \quad (8)$$

$$Y_2(s) = \frac{k_l}{s + 1/\tau_{o2}} \left[ \frac{1}{\tau_{a1}} X_2(s) + X_2^*(s) \right] \quad (9)$$

By linearization of the equilibrium relation, at each of the two stages conditions, and Laplace transformation of the corresponding deviation equations, the following equations were obtained:

$$Y_1(s) = M_1 X_1^*(s) \quad (10)$$

$$Y_2(s) = M_2 X_2^*(s) \quad (11)$$

where:

$$M_1 = \frac{C(B - Y_{1s})}{1 + CX_{1s}^*}$$

$$M_2 = \frac{C(B - Y_{2s})}{1 + CX_{2s}^*}$$

$$\tau_{a1} = \frac{H_1}{A_1}$$

$$\tau_{a2} = \frac{H_2}{A_1}$$

$$\tau_{o1} = \frac{L_1}{O_2}$$

$$\tau_{o2} = \frac{L_2}{O_1}$$

$$\frac{1}{\tau_1} = \frac{1}{\tau_{a1}} + k_h$$

$$\frac{1}{\tau_2} = \frac{1}{\tau_{a2}} + k_h$$

$$k_h = k_{h1} = k_{h2}$$

$$\text{and } k_l = k_{l1} = k_{l2}$$

To carry out stimulus - response test, by considering a step increase in solute concentration in aqueous phase; equations (6) to (11) are rearranged to give:

$$X_1(s) = \frac{1}{\tau_{a1}} \frac{(s + 1/\tau_{23})(s^2 + as + b)}{(s^4 + ds^3 + es^2 + fs + g)} X_i(s) \quad (12)$$

$$X_1^*(s) = \frac{k_l}{M_1 \tau_{a1}} \frac{(s^2 + as + b)}{(s + 1/\tau_{23})(s^4 + ds^3 + es^2 + fs + g)} X_i(s) \quad (13)$$

$$Y_1^*(s) = \frac{k_l}{\tau_{a1}} \frac{(s^2 + as + b)}{(s + 1/\tau_{23})(s^4 + ds^3 + es^2 + fs + g)} X_i(s) \quad (14)$$

$$X_2(s) = \frac{1}{\tau_{a1} \tau_{a2}} \frac{(s + 1/\tau_{22})(s + 1/\tau_{23})}{(s^4 + ds^3 + es^2 + fs + g)} X_i(s) \quad (15)$$

$$X_2^*(s) = \frac{1}{M_2 \tau_{a1} \tau_{a2}} \frac{(s + 1/\tau_{23})}{(s^4 + ds^3 + es^2 + fs + g)} X_i(s) \quad (16)$$

and finally:

$$Y_2(s) = \frac{k_l}{\tau_{a1} \tau_{a2}} \cdot \frac{(s + 1/\tau_{23})}{(s^4 + ds^3 + es^2 + fs + g)} \cdot X_i(s) \quad (17)$$

where,

$$\begin{aligned} a &= T_2 + T_{22} & b &= T_2 \cdot T_{22} + \frac{k_l \cdot k_h}{M_2} & c &= b + \frac{1}{\tau_{a1} \tau_{a2}} & d &= T_1 + T_{23} + a \\ e &= T_1 T_{23} + a(T_1 + T_{23}) + b - T & f &= a T_1 T_{23} + b(T_1 + T_{23}) + a T \\ g &= b T_1 T_{23} - c T & \frac{1}{\tau} &= \frac{k_h \cdot k_l}{M_1} = T & T_1 &= \frac{1}{\tau_{a1}} + k_h & T_2 &= \frac{1}{\tau_{a2}} + k_h \\ \frac{1}{\tau_{23}} &= \frac{1}{\tau_{a1}} + \frac{k_l}{M_1} = T_{23} & \frac{1}{\tau_{22}} &= \frac{1}{\tau_{a2}} + \frac{k_l}{M_2} = T_{22} \end{aligned}$$

For a step stimulus in  $X_i(t)$  with signal gain equals D gm/l. Laplace transform is given by

$$X_i(s) = \frac{D}{s} \quad (18)$$

Inserting equation (18) into equations (12) to (17) gives the Laplace transformation for the system under test. The inverse transformations were obtained and the resulting equations are:

$$X_1(t) = R_1[A_1e^{-r_1t} + A_2e^{-r_2t} + A_3e^{-r_3t} + A_4e^{-r_4t} + A_5] \quad (19)$$

$$X_1^*(t) = R_2[BBe^{-\frac{t}{\tau_{23}}} + B_1e^{-r_1t} + B_2e^{-r_2t} + B_3e^{-r_3t} + B_4e^{-r_4t} + B_5] \quad (20)$$

$$Y_1(t) = R_3[CCe^{-\frac{t}{\tau_{23}}} + C_1e^{-r_1t} + C_2e^{-r_2t} + C_3e^{-r_3t} + C_4e^{-r_4t} + C_5] \quad (21)$$

$$Y_2(t) = R_4[D_1e^{-r_1t} + D_2e^{-r_2t} + D_3e^{-r_3t} + D_4e^{-r_4t} + D_5] \quad (22)$$

$$X_2(t) = R_5[E_1e^{-r_1t} + E_2e^{-r_2t} + E_3e^{-r_3t} + E_4e^{-r_4t} + E_5] \quad (23)$$

$$X_2^*(t) = R_6[F_1e^{-r_1t} + F_2e^{-r_2t} + F_3e^{-r_3t} + F_4e^{-r_4t} + F_5] \quad (24)$$

where  $r_i$ ,  $i = 1, 4$  are the roots of the fourth order polynomial:

$$s^4 + ds^3 + es^2 + fs + g$$

which were obtained by Mathematica Package.

The constants  $A_i$ ,  $B_i$ ,  $C_i$ ,  $D_i$ ,  $E_i$ ,  $F_i$ ,  $i = 1, 5$ ,  $R_j$ ,  $j = 1, 6$  in addition to CC and BB are given in the Annex, as obtained by partial fractions method.

## RESULTS AND DISCUSSIONS

In this study, the aqueous feed is considered as the manipulated variable. Both the effect of its initial concentration and flow rate on the behaviour of the system are considered. The reference values of the parametric study are shown in table (1).

Table (1)

$X_i$ gm/lit.	A Lit/min	O	$L_1$	$L_2$	$H_1$ Lit.	$H_2$
300	0.1	0.2	2.0	2.0	1.0	1.0

When the system is tested by a step signal in feed concentration with signal gain of 50 gm/lit, the roots of the inverse transfer equations are listed in table (2).

Table (2)

parameter	value	Roots			
		$r_1$	$r_2$	$r_3$	$r_4$
$X_i$ gm/lit	100	-46.149	-3.7208	-0.109	-0.091
	200	-35.615	-7.0647	-0.112	-0.087
	300	-26.151	-12.155	-0.113	-0.086
	400	-19.137	-18.071	-0.116	-0.083
A lit/min	0.1	-26.151	-12.155	-0.113	-0.086
	0.11	-19.480	-12.059	-0.126	-0.093
	0.12	-14.698	-12.003	-0.139	-0.099
	0.13	-11.969	-11.218	-0.152	-0.105

It is concluded from the table that the system overdamps over the range of the chosen parameters.

### Effect of Initial Concentration

Fig. (2) shows the responses of the two phases in both stages to the stimulus signal. Part (a) shows a first order behaviour for the response of  $X_i$  to the test. This is in agreement with expectation. The investigation of the transfer function, equation (12) explains that the difference in the power of the polynomials of both denominator and numerator equals 1. For  $X_2$ , this difference equals 2 as predicted from equation (15). A general relation for the order of aqueous phase can be represented by

$$N_A = n$$

where  $n$  : order of transfer function

A : refer to aqueous phase.

For  $Y_1$  and  $Y_2$ , the differences equal three. At the same time part (b) shows a behaviour of a first order system. This is because the reaction is a fast one. The values of the roots and preexponential constants control this effect. It is clear from the figure that the response of second stage organic phase is greatly affected by the test. This is because of the ability of fresh solvent to extract much more solute. At the same time, the organic phase in the first stage is constraint by the maximum loading capacity of the solvent. The aqueous phase in both stages are slightly affected by the test, because of the ability of the solvent for extraction.

### Effect of Feed Flowrate

Figure (3) explains the response to test. Part (a) shows that increasing the flow rate slightly affect  $X_1$  and  $X_2$  at the beginning and the end of the test, with sensible variation at the middle. These differences appear as a result of variation of the slope of the operating line on Mckabe-Thiele diagram. The response of  $Y_1$  to the test is negligible, while it is obvious for the value of  $Y_2$ . The ability of fresh solvent entering the second stage for extraction explains the total system behaviour.

## CONCLUSIONS

The study showed that the extractive interacting system could be represented by a set of O.D.E.s. Laplace transform method is used to solve the model and it is then tested by a step increase in feed concentration. The stimulus response test shows a stable behaviour over the practical range of operating parameter which includes initial concentration and feed flowrate. A general relation for the order of the behaviour of aqueous phase at any stage was concluded.

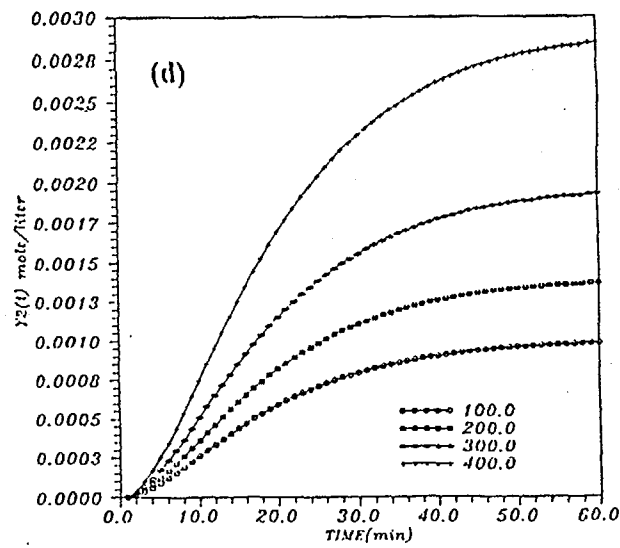
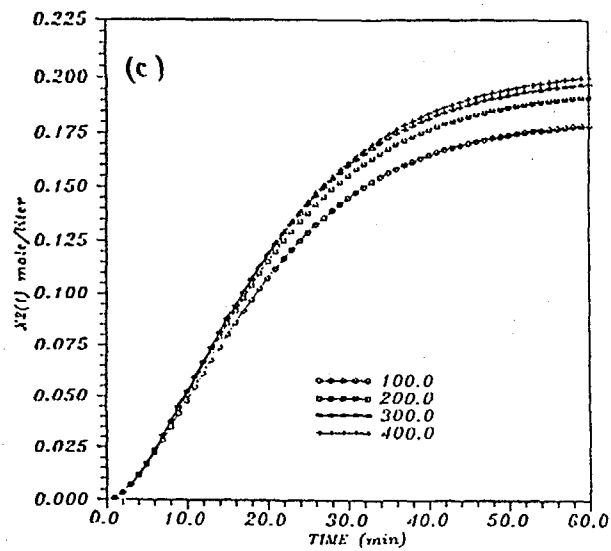
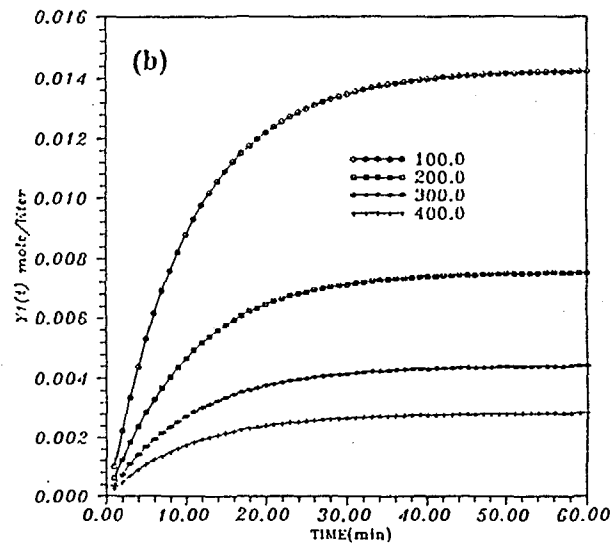
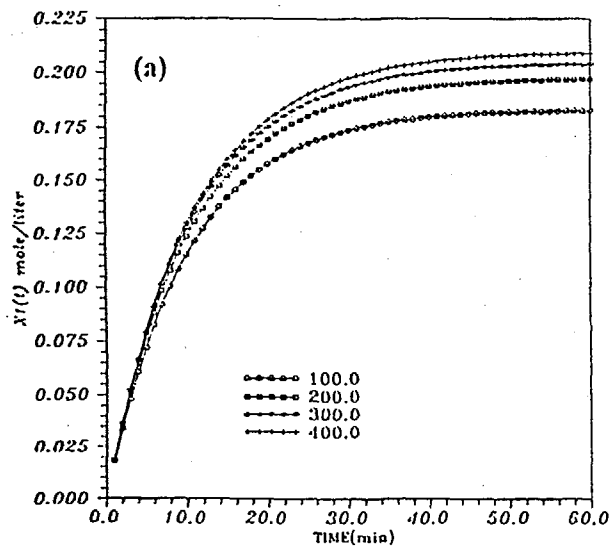


Fig. (2) : Effect of initial feed concentration.

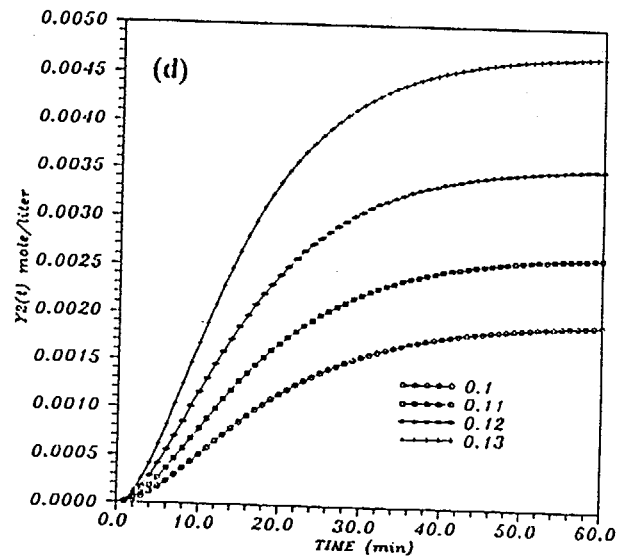
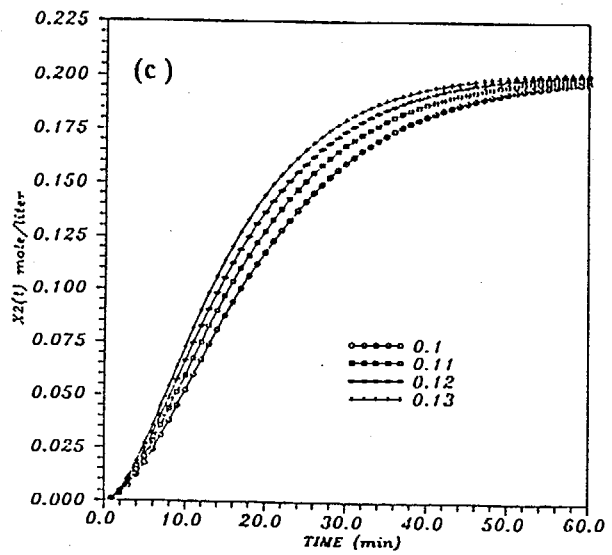
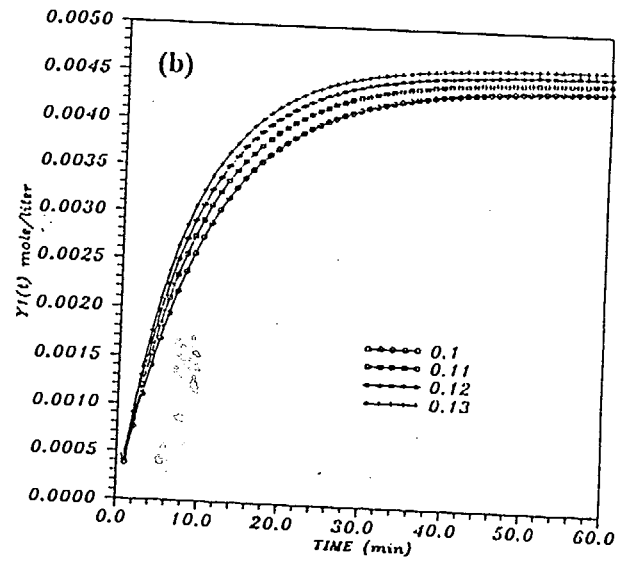
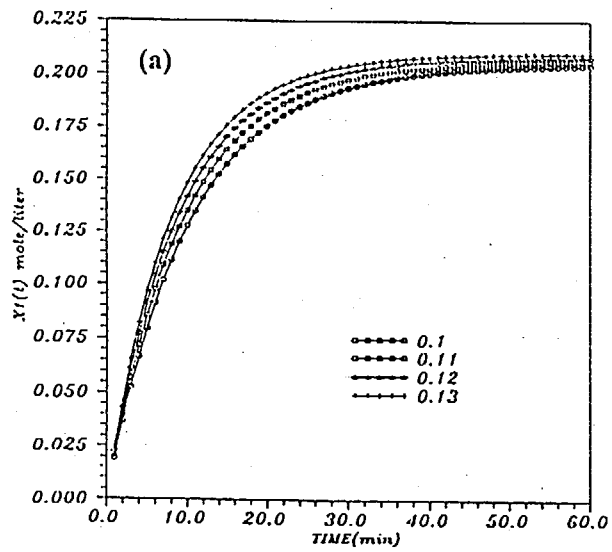


Fig. (3) : Effect of feed flowrate.

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## REFERENCES

- (1) H. Ikeda and R. Kiyose; J. Nucl. Sci. tech.; 18, 558 (1981).
- (2) M.A. El-Rifai; Chem. Eng. Sci.; 30, 79 (1975).
- (3) J.T. lowe; Ind. Eng. Chem. Process. Des. Dev; 7, 362 (1968).
- (4) M. R. El-Souroy, A.M. El-Kamash and H.F. Aly; Arab J. Nucl. Sci. & Appl.; 29, 115(1996).
- (5) W.C. Scotten, SOLVEX Computer Code, ORNL (1975).
- (6) D.A. Jone and W.L. Wilkinson; Chem. Eng. Sci.; 28, 1577(1973).
- (7) Y.L. Hwang and F.G. Hellfferich; Chem. Eng. Sci.; 43, 1099(1988).
- (8) M. Dionosi, F.D. Agostine and R. Remitti; PEPSICODE, Annual Symposium on Safeguards and Nuclear Material Management, France 14-16 May (1991).
- (9) A.E. Elsherbiny; M.Sc. Thesis, Cairo University (1996).
- (10) J.C. Biery and D.R. Boylan, I&EC Fundamentals; 2, 44(1963).
- (11) L. Wanng-Horgium; Chin. J. of Nucl. Sci. & Eng., 11, 159(1991).
- (12) H.J. pant, V.N. Yelgoankev, K.T. Sheory and S. K. Ghosh, NAARRI Annual Conference, Bombay (India) 174, 94 (1997).
- (13) S.H. El-Bialy; Arab J. Nucl. Sci. Appl.: No. 2, 33 (2000).
- (14) J. Horn; Ind. Eng. Chem. Process Des. Dev., 23, 603(1984).
- (15) R.L. Moore; The Mechanism of Extraction of Uranium by Tributyl Phosphate, Report 3196, AECL (1951)



ANNEX

Constants of Inverse Transform Equations

$$A_1 = \frac{(\tau_{23} - r_1)(r_1^2 - Ar_1 + B)}{(r_2 - r_1)(r_3 - r_1)(r_4 - r_1)(-r_1)}$$

$$A_2 = \frac{(\tau_{23} - r_2)(r_2^2 - Ar_2 + B)}{(r_1 - r_2)(r_3 - r_2)(r_4 - r_2)(-r_2)}$$

$$A_3 = \frac{(\tau_{23} - r_3)(r_3^2 - Ar_3 + B)}{(r_1 - r_3)(r_2 - r_3)(r_4 - r_3)(-r_3)}$$

$$A_4 = \frac{(\tau_{23} - r_4)(r_4^2 - Ar_4 + B)}{(r_1 - r_4)(r_2 - r_4)(r_3 - r_4)(-r_4)}$$

$$A_5 = \frac{\tau_{23}B}{r_1r_2r_3r_4}$$

$$B_1 = \frac{(r_1^2 - Ar_1 + C)}{(r_2 - r_1)(r_3 - r_1)(r_4 - r_1)(-r_1)}$$

$$B_2 = \frac{(r_2^2 - Ar_2 + C)}{(r_1 - r_2)(r_3 - r_2)(r_4 - r_2)(-r_2)}$$

$$B_3 = \frac{(r_3^2 - Ar_3 + C)}{(r_1 - r_3)(r_2 - r_3)(r_4 - r_3)(-r_3)}$$

$$B_4 = \frac{(r_4^2 - Ar_4 + C)}{(r_1 - r_4)(r_2 - r_4)(r_3 - r_4)(-r_4)}$$

$$B_5 = \frac{C}{r_1r_2r_3r_4}$$

$$BB = CC$$

$$C_1 = \frac{(r_1^2 - Ar_1 + C)}{(r_2 - r_1)(r_3 - r_1)(r_4 - r_1)(-r_1)}$$

$$C_2 = \frac{(r_2^2 - Ar_2 + C)}{(r_1 - r_2)(r_3 - r_2)(r_4 - r_2)(-r_2)}$$

$$C_3 = \frac{(r_3^2 - Ar_3 + C)}{(r_1 - r_3)(r_2 - r_3)(r_4 - r_3)(-r_3)}$$

$$C_4 = \frac{(r_4^2 - Ar_4 + C)}{(r_1 - r_4)(r_2 - r_4)(r_3 - r_4)(-r_4)}$$

$$C_5 = \frac{C}{r_1r_2r_3r_4}$$

$$CC = \frac{\frac{1}{\tau_{23}^2} - \frac{a}{\tau_{23}} + c}{(r_1 - \frac{1}{\tau_{23}})(r_2 - \frac{1}{\tau_{23}})(r_3 - \frac{1}{\tau_{23}})(r_4 - \frac{1}{\tau_{23}})(r_1 - \frac{1}{\tau_{23}})(\frac{1}{\tau_{23}})}$$

$$D_1 = \frac{(\tau_{23} - r_1)}{(r_2 - r_1)(r_3 - r_1)(r_4 - r_1)(-r_1)}$$

$$D_2 = \frac{(\tau_{23} - r_2)}{(r_1 - r_2)(r_3 - r_2)(r_4 - r_2)(-r_2)}$$

$$D_3 = \frac{(\tau_{23} - r_3)}{(r_1 - r_3)(r_2 - r_3)(r_4 - r_3)(-r_3)}$$

$$D_4 = \frac{(\tau_{23} - r_4)}{(r_1 - r_4)(r_2 - r_4)(r_3 - r_4)(-r_4)}$$

$$D_5 = \frac{\tau_{23}}{r_1r_2r_3r_4}$$

$$E_1 = \frac{(\tau_{22} - r_1)(\tau_{23} - r_1)}{(r_2 - r_1)(r_3 - r_1)(r_4 - r_1)(-r_1)}$$

$$E_2 = \frac{(\tau_{22} - r_2)(\tau_{23} - r_2)}{(r_1 - r_2)(r_3 - r_2)(r_4 - r_2)(-r_2)}$$

$$E_3 = \frac{(\tau_{22} - r_3)(\tau_{23} - r_3)}{(r_1 - r_3)(r_2 - r_3)(r_4 - r_3)(-r_3)}$$

$$E_4 = \frac{(\tau_{22} - r_4)(\tau_{23} - r_4)}{(r_1 - r_4)(r_2 - r_4)(r_3 - r_4)(-r_4)}$$

$$E_5 = \frac{\tau_{22}\tau_{23}}{r_1 r_2 r_3 r_4}$$

$$F_1 = \frac{(\tau_{23} - r_1)}{(r_2 - r_1)(r_3 - r_1)(r_4 - r_1)(-r_1)}$$

$$F_2 = \frac{(\tau_{23} - r_2)}{(r_1 - r_2)(r_3 - r_2)(r_4 - r_2)(-r_2)}$$

$$F_3 = \frac{(\tau_{23} - r_3)}{(r_1 - r_3)(r_2 - r_3)(r_4 - r_3)(-r_3)}$$

$$F_4 = \frac{(\tau_{23} - r_4)}{(r_1 - r_4)(r_2 - r_4)(r_3 - r_4)(-r_4)}$$

$$F_5 = \frac{\tau_{23}}{r_1 r_2 r_3 r_4}$$

$$R_1 = \frac{D}{\tau_{a1}}$$

$$R_2 = \frac{Dk_1}{M_1 \tau_{a1}}$$

$$R_3 = \frac{k_1 D}{\tau_{a1}}$$

$$R_4 = \frac{D}{\tau_{a1} \tau_{a2}}$$

$$R_5 = \frac{Dk_1}{M_2 \tau_{a1} \tau_{a2}}$$

$$R_6 = \frac{Dk_1}{\tau_{a1} \tau_{a2}}$$