Physical Sciences

KINETICS OF SOLVENT EXTRACTION OF ZIRCONIUM (IV) FROM CHLORIDE MEDIUM BY D2EPHA IN KEROSENE USING THE LEWIS CELL TECHNIQUE: A COMPARISON WITH SINGLE DROP TECHNIQUE

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The kinetics of the title system has been investigated by the Lewis cell technique for 1-day ageing of the aqueous phase and compared with those obtained from the single drop technique. The mass transfer flux equations for Zr(IV) have been derived for three aqueous acidities of 0.10, 1 and 5 mol dm^{-3} HCl, respectively, as: J (kmol m^{-2}s^{-1} = 10$^{-5.53\pm0.04}$ $(1+0.00038[Zr(IV)]^{-1})^{-1}$ $[H^+][H_2A_2]_{(o)}$ $(1+0.70[Cl^-])$, J (kmol m^{-2}s^{-1}) = 10$^{-5.80\pm0.02}$ $1+0.004$ $[Zr(IV)]^{-1})^{-1}$ $[H_2A_2]_{(o)}$ $[Cl^-]$ and J (kmol m^{-2} s^{-1}) = 10$^{-6.58\pm0.03}$ $(1+0.0038$ $[Zr(IV)]^{-1})^{-1}$$[H]^+[H_2A_2]_{(o)}$$[Cl^-]$. The values of E_a (kJ mol^{-1}) in kinetic and diffusion regimes are 92 & 14.7 and 84 & 15 for 1 and 5 mol dm^{-3} HCl systems, respectively. For 0.10 mol dm^{-3} HCl system, E_a value cannot be measured for kinetic regime but its value is 15 kJ mol^{-1} in diffusion regime. At intermediate controlled regime (Zr(IV) $\approx$ 3 mmol dm^{-3}), E_a value varies from 11, 12 and 12 kJ mol^{-1} to 42, 105 and 108 kJ mol^{-1} respectively, for 0.10, 1 and 5 mol dm^{-3} HCl systems on varying the temperature from 318 K to 288 K.On the basis of these data, the mechanisms of extraction in different conditions have been suggested.

Key words: Extraction kinetics, Zr(IV), D2EHPA, Lewis cell, Kerosene HCl interface.

Introduction

The extraction equilibria of the Zr(IV)-Cl- D2EHPA-kerosene system has been reported (Biswas and Hayat 2002a). Extraction equilibria have been found to be complicated by the slow change in the composition of the extractable aqueous Zr(IV) species on ageing and variation of the aqueous phase acidity. It is found that the equilibrium data for 1-day ageing can be justified well if the existences of $[Zr_8(OH)_{20}(H_2O)_{24}Cl_{12}]$ in 0.10 mol dm^{-3} HCl medium (Singhal *et al* 1996), $Zr_4(OH)_8(H_2O)_{16}$ $Cl_6]^{2+}$ in 1 mol dm^{-3} HCl medium (Singhal *et al* 1996) and Zr $(H_2O)_5Cl_3]^+$ in 5 mol dm^{-3} HCl medium (Hannane *et al* 1990) are considered to take part in extraction equilibration reactions. On ageing for 30 days, the above species take up 1, 2 and 3 chloride ions, respectively. For 1-day ageing, the extraction equilibrium constants have been estimated to be 10$^{-5.0}$, 10$^{-4.1}$ and 10$^{-3.4}$ for 0.10, 1 and 5 mol dm^{-3} HCl systems, respectively.

In another paper (Biswas and Hayat 2002b), the kinetics of the titled system of 1-day ageing has been measured by the single drop technique. The rate constants have been measured to be 10$^{-5.37}$, 10$^{-5.77}$ and 10$^{-6.62}$ for 0.1, 1 and 5 mol dm^{-3} HCl systems, respectively. According to Danesi and Chiarizia (1980), a change in the experimental technique and concentration

condition may alter a kinetic regime to a diffusional regime or mixed control or vice versa. Now, it is established that not only the concentration term, but also the temperature condition alters the mechanism of extraction (Hughes and Biswas 1991 and 1993; Biswas and Begum 2000; Biswas and Mondal 2003). This paper discusses the kinetics of the Zr(IV) extraction from Cl- medium of 1-day ageing by D2EHPA in kerosene by the lewis cell technique to compare these results with those obtained from the single drop technique.

Experimental

Reagents. D2EHPA was procured from BDH (98% purity) and used as such. As a source of Zr(IV), octahydrated zirconyl chloride (M.C and Bell, 98%) was used. Kerosene was bought from the local market and redistilled to collect the fraction distilling over 220-260°C. It was mostly colorless and aliphatic in nature. All other chemicals were of reagent grade and used without further purification.

Analytical. The concentration of Zr(IV) in the aqueous phase was estimated by the EDTA-pyrocatechol violet method (Charlot 1964) at 590 nm using a WPA S104 spectrophotometer. For pH adjustment of the aqueous solution of Zr(IV) required in the above method (pH5.2), a Mettler Toledo 320 pH meter was used.

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*Cell and technique.*The construction of Lewis cell and operating technique are given elsewhere (Biswas *et al* 1998). Identical aliquots (100 cm^{-3}) of aqueous and organic solutions (pre-thermostated) can be taken in the cell without much disturbing the interface and allowed for mass transfer for a definite time. An electrical stirrer having two 1 cm blades stirs the organic phase clockwise and a magnetic stirrer (2 cm long capsule) is used to rotate the lower aqueous phase in the same direction. The speed of stirrer is controlled at 2.5 Hz maximum without disturbing the interface. After 2-6 min, 2 cm^3 aqueous phase is taken out for analysis. The amount of Zr(IV) transferred into the organic phase can be estimated from the analysis and varies within ± 1%. All experiments have been carried out at $(30 \pm 1)°$C, otherwise stated. The interfacial area in all experiments is kept at 3.37 x 10^{-3} m^2, otherwise mentioned, which can be altered by setting circular plastic rings within the cell where interface is formed.

*Preparation of the aqueous solution.*The aqueous solution containing definite amounts of Zr(IV), Cl$^-$ and H$^+$ are prepared and aged exactly for 24 h before being used in the cell for extraction rate study.

Notations, abbreviations and subscripts.

a,b,c,d,	=	orders with respect to Zr(IV), H$^+$, H$_2$A$_2$ and C1$^-$ concentrations, respectively
$\overset{a}{a}_{Zr(IV)}$	=	amount of Zr(IV) transferred in 100 cm^3 organic phase through interface A in time t, kmol
A	=	interfacial area through which mass transfer occurs, m^2
A	=	frequency factor
D	=	diffusion coefficient, m^{2}s^{-1}
D2EHPA	=	di-2-ethylhexylphosphoric acid
E$_a$	=	activation energy, kJ mol^{-1}
h	=	higher temperature or concentration region
H$_2$A$_2$	=	dimeric D2EHPA
J	=	mass transfer flux, kmol m^{-2}s^{-1}
k$_f$	=	forward extraction rate constant, unit depends on the concentration region Zr(IV) and C1$^-$
K$_{Zr}$	=	proportionality constant of Zr(IV) concentration term in rate equation, mol dm^{-3}
K$_{cl}$	=	proportionality constant of Cl$^-$ concentration term in rate equation, dm^3 mol^{-1}
l	=	lower temperature or concentration region
r	=	radius of diffusing species
t	=	time allowed for mass transfer through interface, S
T	=	temperature, K
x	=	concentration change of Zr(IV) in the aqueous phase, mg dm^{-3}

η	=	coefficient of viscocity, cp
(ini)	=	initial
(o)	=	organic phase

*Treatment of experimental data.*If x (mg dm^{-3}) is the concentration change of Zr(IV) in the aqueous phase, then (x /10) mg of Zr(IV) will be transferred into the organic phase provided 100 cm^3 each phase being used in the cell. If t (s) represents the time during which mass transfer occurs, the mass transfer flux of Zr(IV) can be calculated from the following relationship:

$$J(\text{kmol m}^{-2}\text{s}^{-1}) = (10^{-7} x) / (91.22 \text{ x } 3.368 \text{ x } t) \dots\dots\dots\dots\dots\dots (1)$$

In a single-run, the x vs t plots generally hold almost straight line relationship during the initial periods of extraction. After the lapse of some period, the rate of variation of x with t is decreased. Since for small t-values, the values fo x are very small, the calculated J-values are not found to be reproducible. So J-values have been calculated for Δ t = (4-0) x 60s, (8-4) x 60s, (12-8) x 60s, (16-12) x 60s, and (20-16) x 60s and the averages of J-values have always been taken.

At a constant temperature and phase agitaion, J is related to concentration terms as:

$$J = k_f [\text{Zr(IV)}]^a [\text{H}^+]^b [\text{H}_2\text{A}_2]^c {}_{(o)}[\text{Cl}^-]^d\dots\dots\dots\dots\dots\dots\dots\dots\dots (2)$$

Which can be rewritten as:

$$\log J = \log k_f + a \log[\text{Zr(IV)}] + b \log[\text{H}^+] + c \log[\text{H}_2\text{A}_2]_{(o)}$$
$$+ d \log [\text{Cl}^-] \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (3)$$

Equation (3) can be used to evaluate the reaction orders (a, b, c and d) and rate constant (k$_f$). If the concentrations of the variables are kept constant, the slop of logJ vs log[4th variable] will give the reaction order with respect to the fourth variable concentration. From the intercept of the plots, the value of k$_f$ can be evaluated. The temperature dependence data can be treated by the Arrhenius theory.

Results and Discussion

Fig 1 shows the variation of the amount of mass transfer, a$^o_{Zr(IV)}$ and flux on the interfacial area used in the Lewis cell. It is found that the mass transfer amount is directly proportional to interfacial area, but the flux is independent of interfacial area. In subsequent experiments, the cell with interfacial area of 3.37 x 10^{-3} m^2 has been used.

The variation of mass flux of Zr(IV) on its concentration for 1 mol dm^{-3} HCl system ([Cl$^-$] = 3 mol dm^{-3}) is shown in Fig 2. The experimental points do not fall on a straight line. The solid line is theoretical and represented by:

$logJ = -6.85 - log (1+K_{Zr}[Zr(IV)]^{-1})$ .... (4)

Whereas, the dashed with doted line (asymptote at higher concentration region of Zr(IV) is:

$log J = log k_f [H^+]^b [H_2A_2]^c_{(o)} [Cl^-]^d = -6.86$ .... (5)

and the dashed line (asymptote at lower concentration region of Zr(IV)is:

$log J = -6.85 - logK_{Zr} + log[Zr(IV)]$ .... (6)

At the point of intersection of Eqs. (5) and (6), $-logK_{Zr} + log [Zr(IV)] = 0$, which gives K_{Zr} as 0.004.

Similar, plots for 0.10 and 5 mol dm^{-3} systems are given in Fig 3. For 0.10 mol dm^{-3} HCl system, the solid line is represented by:

$log J = -7.71 - log (1 + 0.00038[Zr(IV)]^{-1})$ .... (7)

and for 5 mol dm^{-3} HCl system, the solid line represents:

$log J = - 6.9 - log (1 + 0.0038[Zr(IV)]^{-1})$ .... (8)

The dependences of mass transfer flux of Zr(IV) on the aqueous phase acidity at constant chloride concentration of either 3 (for [HCl]< 3 mol dm^{-3}) or 5 mol dm^{-3} (for [HCl] = 2-5 mol dm^{-3}) are shown in Fig 4. Similar results are obtained for all extractant concentrations used. Within 0.30 to 3 mol dm^{-3} HCl region ([Cl$^-$] = 3 mol dm^{-3}), the flux is independent of H$^+$ concentration. But the flux is directly proportional to hydrogen ion concentration in its higher and lower concentration regions.

The variation of flux with the variation of extractant concentration is displayed in Fig 5. In all cases, straight lines of unity slopes are obtained. So, the rate of extraction is directly proportional to extractant concentration in the organic phase. The results of the chloride dependence study are given in Fig 6. For H$^+$ concentrations of 1 and 5 mol dm^{-3}, the rate of extraction is proportional to chloride ion concentration in the aqueous phase. For 0.10 mol dm^{-3} H$^+$ concentration, the flux varies according to the following relationship:

$logJ = log k_f (1 + 0.00038[Zr(IV)]^{-1})^{-1}[H^+][H_2A_2]_{(o)} + log (1 + K_{cl} [Cl^-])$ .... (9)

Where, K_{cl} is estimated to be 0.70 by the curve-fitting method. From the intercepts of the straight lines, asymptotes or tangents in Fig 2-6, the values of rate constant (k_f) at 303 K have been evaluated (Table1). The average values of logk_f are $10^{-5.53\pm0.04}, 10^{-5.80\pm0.02}$ and $10^{-6.58\pm0.03}$ for 0.10, 1 and 5 mol dm^{-3} HCl systems, respectively. Units of k_f depend on the concentration regions of H$^+$, Zr(IV) and Cl$^-$.

Fig 7, shows the temperature dependence of flux in the intermediate control regime of Zr(IV) concentration. In all acidities of the aqueous phase, Arrhenius plots are not straight lines. In lower temperature region under investigations, the E_a values are over 100 kJ mol^{-1} for 1 and 5 mol dm^{-3} HCl systems, whereas, it is about 42 kJ mol^{-1} for 0.10 mol dm^{-3} HCl system. These values in the higher temperature region of investigation are 12, 11 and 11 kJ mol^{-1}, respectively. Fig 8 shows the Arrhenius plots in the kinetic and diffusion regions of Zr(IV) concentration. At all aqueous acidities, E_a values are about 14.5 kJ mol^{-1} in diffusion regime and over 80 kJ mol^{-1} in the kinetic regime.

From the above experimental results, the mass transfer flux of Zr(IV) for 5, 1 and 0.10 mol dm^{-3} HCl systems derived from the Lewis cell technique at 303 K, respectively, are as follow:

$J = 10^{-6.58\pm0.03}(1 + 0.0038 [Zr(IV)]^{-1})^{-1}[H^+][H_2A_2]_{(o)}[Cl^-]$ ....(10)

$J = 10^{-5.80\pm0.02}(1 + 0.004 [Zr(IV)]^{-1})^{-1}[H_2A_2]_{(o)}[Cl^-]$.................. (11)
and
$J = 10^{-5.53\pm0.04}(1+0.00038 [Zr(IV)]^{-1})^{-1} [H^+][H_2A_2]_{(o)} (1+0.7 [Cl^-])$ ....(12)

In comparison to followings, respectively, derived from the single drop technique (Biswas and Hayat 2002a):

$J = 10^{-6.62\pm0.13}(1+0.0056 [Zr(IV)]^{-1})^{-1}[H^+][H_2A_2]_{(o)}[Cl^-]$ ....(13)

$J = 10^{-5.77\pm0.14}(1+0.0056 [Zr(IV)]^{-1})^{-1}[H_2A_2]_{(o)}[Cl^-]$ ....(14)
and
$J = 10^{-5.37\pm0.10}(1+0.00036 [Zr(IV)]^{-1})^{-1}[H_2A_2]_{(o)}(1+0.69[Cl^-])$....(15)

It is therefore, seen that the rate measurements by the single drop technique and the Lewis cell operated at 2.5 Hz yield almost similar flux equations, with only appreciable change in the value of K_{Zr} (0.0056 from single drop technique and ~0.004 from Lewis cell). The valus of the rate constants are almost unchanged within the vairance limit. So, it is concluded that the single drop (falling) technique and the Lewis cell operated at 2.5 Hz possess comparable hydrodynamic condition to yield similar flux equations. The values of E_a measured from both techniques mentioned are also comparable. Hence the mechanism of extraction in different aqueous acidity regions given from the results obtained by the single falling drop technique (Biswas and Hayat 2002b) will also be applicable to the results obtained by the Lewis cell technique.

In all acidity regions under investigation, the rate of extraction is independent of Zr(IV) concentration in its higher concentration regions and so, the extraction processes are diffusion controlled at higher Zr(IV) concentration regions of Zr(IV). But in the lower concentration region of Zr(IV), the rate is directly proportional to Zr(IV) concentration

and so the processes are chemically controlled. It is found that within Zr(IV) concentration of ~ 4-30 mmol dm^{-3} for 1 and 5 mol dm^{-3} HCl systems and of ~ 0.4 - 3 mmol dm^{-3} for 0.10 mol dm^{-3} HCl system are intermediate controlled. So, the most results collected in this paper are for intermediate controlled process. For 0.10 mol dm^{-3} HCl system, not only the concentration region of Zr(IV) but also the concentration region of Cl^{-} determine the regimes. At low concentration region of Cl^{-}, the process will be diffusion controlled and in the higher concentration region of Cl^{-}, the process will be chemically controlled.

In diffusion controlled processes, the flux equations lack Zr(IV) concentration term and the diffusion of $H_3A_2^+$ (formed by the association of proton with H_2A_2) from the interface to the aqueous film of the interface is the slowest step. This is supported by low E_a value(~ 14 kJ mol^{-1}). It is known that for diffusion controlled process the activation energy is below 20 kJ mol^{-1} (Habashi 1968). In lower concentration region of Zr(IV), the following chemical reactions have been suggested for 0.10, 1 and 5 mol dm^{-3} HCl system, respectively, as rate determining (Biswas and Hayat 2002b):

$$[Zr_8(OH)_{20}(H_2O)_{24}Cl_{12}]_{(i)}+H_3A_2Cl_{(i)} \rightarrow [Zr_8(OH)_{20}(H_2O)_{24}Cl_{13}]^{-}[H_3A_2]^+_{(i)} \quad \text{...(16)}$$

$$[Zr_4(OH)_8(H_2O)_{16}Cl_7]^+_{(i)}+H_2A_{2(i)} \rightarrow [Zr_4(OH)_8(H_2O)_{16}Cl_7.H_2A_2]^+_{(i)} \quad \text{...(17)}$$

$$[Zr(H_2O)_5Cl_3]^+_{(i)}+H_3A_2Cl_{(i)} \xrightarrow{-H_2O} [Zr(H_2O)_4Cl_4.H_3A_2]^+ \quad \text{..... (18)}$$
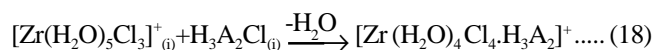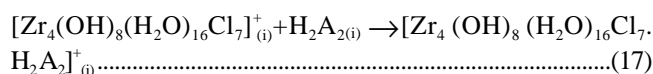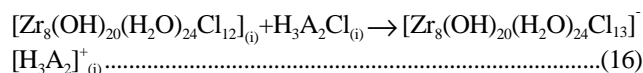
These chemically rate determining steps are supported by the high E_a values (> 80 kJ mol^{-1}) since for chemically controlled process the E_a value is over 50 kJ mol^{-1} (Habashi 1968).
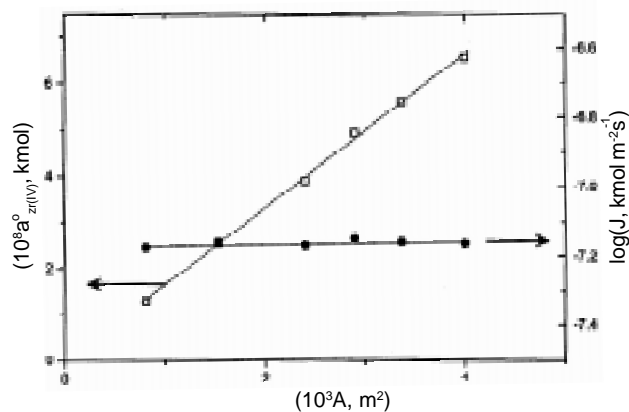

Fig 1. Dependence of the amount of mass transfer and flux on interfacial area. [Zr(IV)]$_{(ini)}$ = 3.60 mmol dm^{-3}, [HCl] = 1 mol dm^{-3} ; [H$_2$A$_2$]$_{(o)}$ = 0.03 mol dm^{-3} ; [Cl$^-$] = 3 mol dm^{-3}; Δt = 240 s ; ageing time = 1-day; temp. = (30±1)$^{\circ}$C.
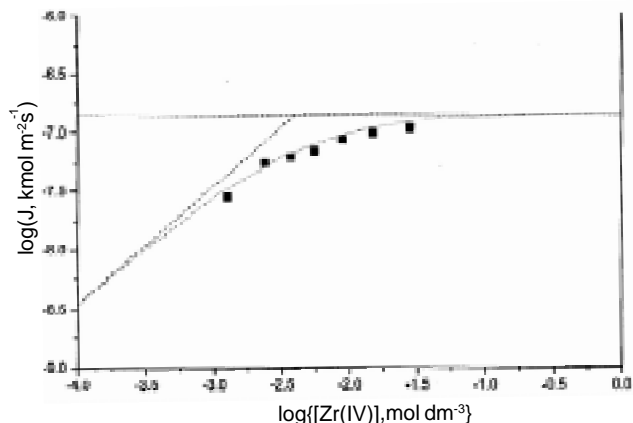

Fig 2. Dependence of the mass flux of Zr(IV) on its concentration in the intermediate acidity region of the aqueous phase. [HCl] = 1 mol dm^{-3} ; [H$_2$A$_2$]$_{(o)}$ = 0.03 mol dm^{-3} ; [Cl$^-$] = 3 mol dm^{-3} ; Δt = 240 s ; ageing time =1-day ; temp. = (30±1)$^{\circ}$C.

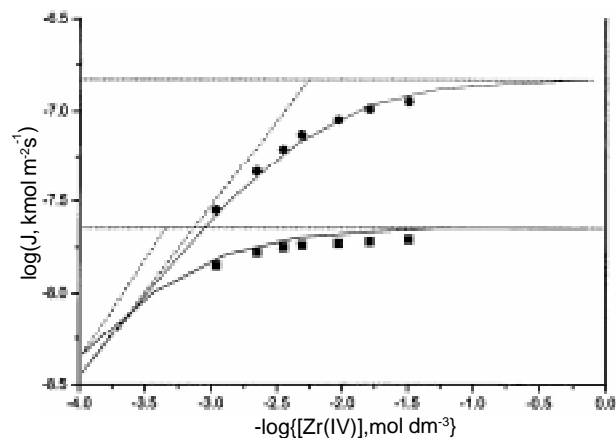**Fig 3.** Dependence of the mass flux of Zr(IV) concentration in lower and higher concentration regions of hydrochloric acid in the aqueous phase. [HCl] = 0.1 mol dm^{-3} ;(■) and 5 mol dm^{-3} (●) ; [H$_2$A$_2$]$_{(o)}$ = 0.02 mol dm^{-3} ; [Cl$^-$] = 3 mol dm^{-3} (●); and 5 mol dm^{-3} (■) ; Δt = 240 s ; ageing time = 1-day ; temp. = (30±1)$^{\circ}$C.

Within Zr(IV) concentration of 4-30 mmol dm^{-3} for 5 and 1 mol dm^{-3} HCl system and of 0.4 - 3 mmol dm^{-3} for 0.10 mol dm^{-3} HCl system, the intermediate controlled mechanism is changed with the variation of temperature. The intermediate controlled process becomes diffusion controlled at higher temperature region and chemically controlled at lower temperature region. This is because of the fact that the rate of a chemical reaction is governed by Arrhenius equation, whereas, the rate of diffusion is governed by Stokes-Einstein equation (Habashi 1968). Arrhenius equation ($k_f = Ae^{-Ea/Rt}$) states that if temperature is doubled, the rate of reaction is increased 100 folds but Stokes-Einstein equation (D = RT / 2πηrN) indicates that if tempera-

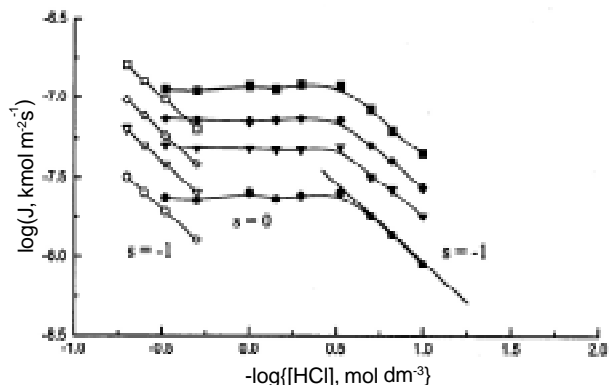**Fig.4.** Dependence of Zr(IV) transfer flux on aqueous acidity. $[Zr(IV)]_{(ini)} = 3.60$ mmol dm^{-3}; $[H_2A_2]_{(o)} = 0.01$ mol dm^{-3} (○, ●); 0.02 mol dm^{-3} (▽, ▼); 0.03 mol dm^{-3} (◇, ◆); 0.05 mol dm^{-3} (□, ■); $[Cl^-] = 3$ mol dm^{-3} (●, ▼, ◆, ■); 5 mol dm^{-3} (○, ▽, ◇, □); ageing time = 1-day; temp. = $(30\pm1)^{\circ}$C.

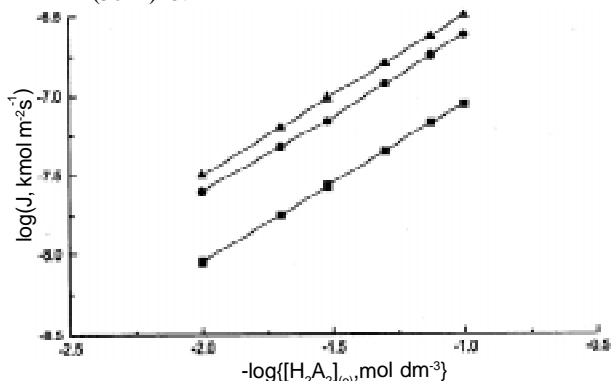**Fig.5.** Dependence of flux on extractant concentration in the organic phase. $[Zr(IV)]_{(ini)} = 3.60$ mmol dm^{-3}; $[HCl] = 0.1$ mol dm^{-3} (■); 1 mol dm^{-3} (●); 5 mol dm^{-3} (▲); $[Cl^-] = 3$ mol dm^{-3} (■, ●); 5 mol dm^{-3} (▲); ageing time = 1-day; temp. = $(30\pm1)^{\circ}$C.
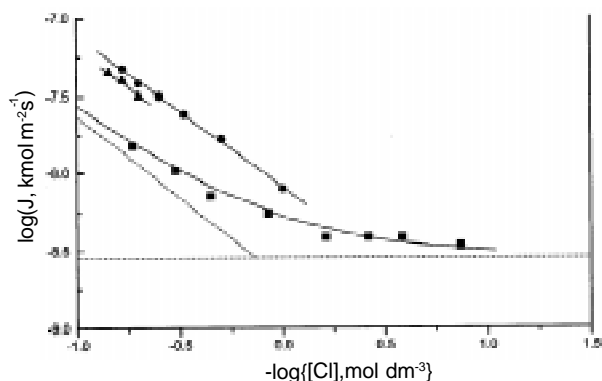

Fig.6. Dependence of flux on chloride ion concentration in the aqueous phase. $[Zr(IV)]_{(ini)} = 3.60$ mmol dm^{-3}; $[HCl] = 0.1$ mol dm^{-3} (■), 1 mol dm^{-3}; (●), 5 mol dm^{-3}; (▲), $[H_2A_2]_{(o)} = 0.01$ mol dm^{-3}; ageing time = 1 day; temp. = $(30\pm1)^{\circ}$C.

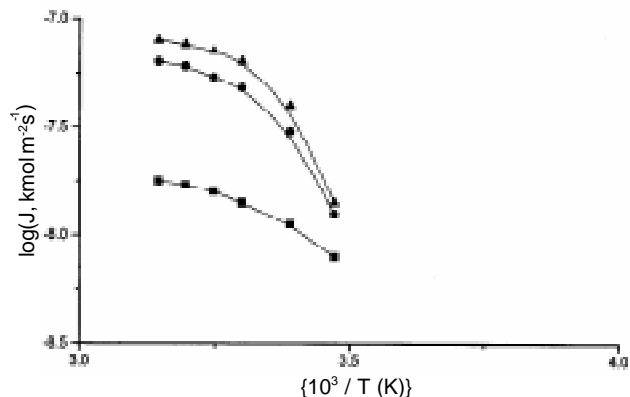**Fig.7.** Dependence of flux on temperature in the intermediate control regime. $[H_2A_2]_{(o)} = 0.02$ mol dm^{-3}; ageing time = 1-day; (■), $[HCl] = 0.1$ mol dm^{-3}; $[Cl^-] = 3$ mol dm^{-3} $[Zr(IV)]_{(ini)} = 1$ mmol dm^{-3}; $E_a^l = 42$ kJ mol^{-1}; $E_a^h = 11$kJ mol^{-1}; (●), $[HCl] = 1$ mol dm^{-3}; $[Cl^-] = 3$ mol dm^{-3}; $[Zr(IV)]_{(ini)} = 3.36$ mmol dm^{-3}; $E_a^l = 105$ kJ mol^{-1}, $E_a^h = 12$ kJ mol^{-1}; (▲), $[HCl] = 5$ mol dm^{-3}; $[Cl^-] = 5$ mol dm^{-3}; $[Zr(IV)]_{(ini)} = 3.36$ mmol dm^{-3}; $E_a^l = 108$ kJ mol^{-1}; $E_a^h = 12$ kJ mol^{-1}.
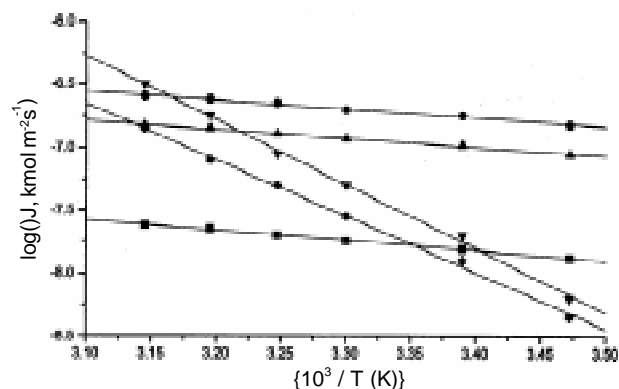

Fig.8. Dependence of flux on temperature kinetic and diffusion regimes. $[H_2A_2]_{(o)} = 0.02$ mol dm^{-3}; ageing time = 1-day. Diffusion regime: (■); $[HCl] = 0.1$ mol dm^{-3}; $[Cl^-] = 3$ mol dm^{-3}; $[Zr(IV)]_{(ini)} = 3.2$ mmol dm^{-3}; $E_a = 14$ kJ mol^{-1}; (●), $[HCl] = 1$ mol dm^{-3}; $[Cl^-] = 3$ mol dm^{-3}; $[Zr(IV)]_{(ini)} = 32$ mmol dm^{-3}; $E_a = 14.7$ kJ mol^{-1}; (▲), $[HCl] = 5$ mol dm^{-3}; $[Cl^-] = 5$ mol dm^{-3}; $[Zr(IV)]_{(ini)} = 32$ mmol dm^{-3}; $E_a = 15$ kJ mol^{-1}. Kinetic regime: (▼), $[HCl] = 1$ mol dm^{-3}; $[Cl^-] = 3$ mol dm^{-3}; $[Zr(IV)]_{(ini)} = 1$ mmol dm^{-3}; $E_a = 92$ kJ mol^{-1}; (◆), $[HCl] = 5$ mol dm^{-3}; $[Cl^-] = 5$ mol dm^{-3}; $[Zr(IV)]_{(ini)} = 1$ mmol dm^{-3}; $E_a = 84$ kJ mol^{-1}.

ture is doubled, the rate of diffusion is doubled. An intermediate controlled process at a particular temperature may be converted to a diffusion controller process solely on rising temperature because of the fact that on increasing temperature, chemical rate is increased much faster than the diffusion rate and so the chemical reaction remains no longer as rate controlling. Conversely, an intermediate controlled process may be converted to a chemically controlled process on decreas-

Table 1
Evaluation of k_f at 303 K for 1-day ageing using Lewis cell technique

Fig. no.	[Zr(IV)], mol dm^{-3}	[H$^+$], mol dm^{-3}	[Cl$^-$], mol dm^{-3}	[H$_2$A$_2$]$_{(o)}$ mol dm^{-3}	Intercept,1	logk$_f$	Average logk$_f$	S.D
(i) For 0.1 mol dm^{-3} HCl system								
3	-	0.1	3.0	0.02	-4.40[l]	-5.61	-5.53	0.04
	-	0.1	3.0	0.02	-7.7[h]	-5.50		
4	0.0036	-	3.0	0.01	-7.08	-5.53		
	0.0036	-	3.0	0.02	-6.60	-5.53		
	0.0036	-	3.0	0.03	-6.60	-5.53		
	0.0036	-	3.0	0.05	-6.45	-5.60		
5	0.0036	0.1	3.0	-	-6.06	-5.51		
6	0.0036	0.1	-	0.01	-8.55[l]	-5.51		
					-8.69[h]	-5.49		
(ii) For 1 mol dm^{-3} HCl system								
2	-	1.0	3.0	0.03	-4.46[l]	-5.82	-5.80	0.02
	-	1.0	3.0	0.03	-6.85[h]	-5.81		
4	0.0036	-	3.0	0.01	-7.60	-5.77		
	0.0036	-	3.0	0.02	-7.32	-5.79		
	0.0036	-	3.0	0.03	-7.16	-5.81		
	0.0036	-	3.0	0.04	-6.39	-5.80		
5	0.0036	1.0	3.0	-	-6.61	-5.78		
6	0.0036	1.0	-	0.01	-8.10	-5.79		
(iii) For 5 mol dm^{-3} HCl system								
3	-	5.0	5.0	0.02	-4.48[l]	-6.60	-6.58	0.03
	-	5.0	5.0	0.02	-6.90[h]	-6.60		
4	0.0036	-	5.0	0.01	-8.10	-6.49		
	0.0036	-	5.0	0.02	-7.90	-6.59		
	0.0036	-	5.0	0.03	-7.72	-6.58		
	0.0036	-	5.0	0.05	-7.50	-6.59		
5	0.0036	5.0	5.0	-	-5.50	-6.59		
6	0.0036	5.0	-	0.01	-8.20	-6.59		

ing the temperature because of the fact that on decreasing temperature, chemical rate is decreased much faster than the diffusion rate and so the diffusion remains no longer as rate controlling.

Conclusion

The rate measurements made by the Lewis cell technique operated at 2.5 Hz give almost identical results with those obtained from the single drop technique and so, the contribution of hydrodynamics to mass flux in both techniques mentioned will be of the same order.

References

Biswas R K, Habib M A, Ali M R, Haque M Z 1998 Kinetics of Mn(II) extraction in the acidic chloride - D2EHPA - kerosene system using the constant interfacial area stirred cell technique. *Pak J Sci Ind Res* **41**(3) 121-127.

Biswas R K, Begum D A 2000 Kinetics of extraction and stripping of Ti(IV) in HCl - D2EHPA - kerosene system using the single drop technique. *Hydrometallurgy* **55** 57-77.

Biswas R K, Hayat M A 2002a Solvent extraction of Zirconium (IV) from chloride media by D2EHPA in kerosene. *Hydrometallurgy* **63** 149-158.

Biswas R K, Hayat M A 2002b Kinetics of solvent extraction of Zirconium(IV) from chloride medium by D2EHPA in kerosene using the single drop technique. *Hydrometallurgy* **65** 205-216.

Biswas R K, Mondal M G K 2003a Kinetics of VO^{2+} extraction by D2EHPA. *Hydrometallurgy* **69** 117-133.

Charlot G 1964 *Colorimetric Determination of Elements*. Elsevier, Amsterdam p 438.

Danesi P R, Chiarizia R 1980 *Critical Reviews in Analytical Chemistry* (Ed. Campbell B) CRC Press, Boca Raton, FL, Chapter 10. p 1-127.

Habashi F 1968 *Principles of Extractive Metallurgy*. Gordon and Breach, New York, USA, **1** p 143.

Hannane S A, Bertin F, Bouix J 1990 Etude de 1'hydrolyse de Zr(IV) per spectrometrie Raman et RMN du proton. 1. Mise en evidence et formulation des especes en solution. *J Bull Soc Chim Fr* **127** 43-49.

Hughes M A, Biswas R K 1991 The kinetics of vanadium(IV) extraction in the acidic sulphate-n-hexane system using the rotating diffusion cell technique. *Hydrometallurgy* **26** 281-297.

Hughes M A, Biswas R K 1993 The kinetics of manganese(II) extraction in the acidic sulphate-D2EHPA-n-hexane system using the rotating duffusion cell technique. *Hydrometallurgy* **32** 209-221.

Singhal A, Toth L M, Lin J S, Affhofter K 1996 Zirconium(IV) tetramer/ octamer hydrolysis equilibrium in aqueous hydrochloric acid. *J Am Chem Soc* **118** 11529-11534.