J. Natn. Sci. Coun. Sri Lanka 1992 **20** *(2) : 301-308*

KINETIC STUDIES ON THE SOLVENT EXTRACTION OF IRON (III) FROM AQUEOUS SOLUTION WITH 1-PHENYL-3-METHYL-4-(P-NITROBENZOYL) PYRAZOL-5-ONE DISSOLVED IN CHLOROFORM : RATE OF BACKWARD EXTRACTION

M.O.C. OGWUEGBU
School of Physical Sciences, Abia State University, P.M.B. 2000, Uturu, Nigeria.

AND

N.C. OFORKA AND A.I. SPIFF
Department of Pure and Industrial Chemistry, University of Port-Harcourt, Nigeria.

(Date of receipt : 22 January 1992)
(Date of acceptance : 06 November 1992)

Abstract: The rate of backward extraction of the tris-(nitropyrazolonato) iron(III) chelate, $Fe(NPz)_3$ from the organic phase has been studied under various conditions. Experimental data show that the rate of stripping iron(III) chelate is first order with respect to $[Fe(NPz)_3]_{org}$ and $[H^+]$, and inverse first order dependent on $[HNPz]_{org}$. The rate of backward extraction is believed to be controlled by the dissociation of the iron(III) monopyrazolonate cation to Fe^{3+} and NPz^-. The rate constant, k_b for the stripping process was determined to be $2.7 \times 10^3 s^{-1}$.

INTRODUCTION

The reactivity of metal ions with various ligands is primarily governed by the values of their ionic potential, z/r, (which denotes the ratio of their ionic charge, z and the ionic radius, r) and the electronic structure of the metal ion. The rate of extracttion of metal ions from aqueous solutions has been reported[1] to be slow when the charge is large and/or the radius is small. This has been attributed to slow substitution of water of hydration.

A large amount of information has appeared in the literature[2-4] on kinetic studies regarding the forward extraction of metal ions from aqueous solutions, while little information has been recorded concerning the kinetic studies of the rate of backward extraction of metal ions from their complexes in the organic phase.[5] More recently are the works of Mirza *et al.*[5] which highlighted the studies of the rate of backward extraction of zirconium pyrazolonate chelate from the organic phase, and of Fleming *et al.*[6,7] which reported kinetic studies of solvent extraction of Fe(III) and Cu(II) from aqueous solution.

The present work was aimed at providing further information on the rate of stripping tris-nitropyrazolonate Fe(III) chelate from the organic chloroform phase to the aqueous phase of various hydrogen ion concentrations.

METHODS AND MATERIALS

Apparatus and Reagents

The nitropyrazolone (HNPz) was synthesized from high grade p-nitrobenzoyl chloride and 1-phenyl-3-methyl-5-pyrazone (HPMP) as described by Jensen[8]and Okafor.[9] However, HPMP was initially prepared from analytical grade phenylhydrazine and ethylacetoacetate.

The HNPz that was previously recrystallized from ethanol was dissolved in chloroform to obtain the desired concentration. All other reagents were of analytical grade, except otherwise stated.

The stock solution of Fe(III) was prepared by dissolving 0.216g of ferric ammonium sulphate, $NH_4Fe(SO_4)_2.12H_2O$ in 250cm^3 of 0.1Mdm^{-3} H_2SO_4 solution giving 1.7x10^{-3} Mdm^{-3} Fe(III). Further dilutions were made there from by adding appropriate amounts of distilled demineralized water and suitable buffer solutions (KCl/HCl and NaAc/HAc) after proper adjustments with H_2SO_4/NH_3 solutions, to attain aqueous buffer medium of pH range 0.5 to 3.2. Spectrophotometric measurements were made using SP8-100 UV-visible spectrophotometer (Pye Unicam, Cambridge U.K.) and the aqueous medium pH values were recorded with TOA Digital pH meter model HIM-208.

Back Extraction Procedure

The backward extraction studies were carried out by first extracting the Fe(III) ions from the organic phase to the aqueous phase, by mixing equal volumes (4cm^3) of 4.5x10^{-5} Mdm^{-3} Fe(III) solution and 0.002-0.05 Mdm^{-3} HNPz chloroform solutions in stoppered extraction bottles. The mixture was agitated at a high constant speed for a specific interval of time (5-240 mins) by means of a mechanical shaker. After extraction, the phases were allowed 30 mins settling time, after which they were separated. The Fe(III)-pyrazolonate organic extract was subsequently agitated with equal volume of aqueous solution for a specific time interval (5-240 mins). The phases were allowed to separate, and the concentration of Fe(III) back-extracted was determined spectrophotometrically[10] using 1,10-phenanthroline at 480 nm, while that in the organic phase as complex was determined by meterial balance.

All experiments were conducted at 26 ± 0.5^{0}C and constant ionic strength of 0.3M, maintained by the use of sodium sulphate. Preliminary experiments showed that sulphate ions had no effect on extractions. The extraction equilibrium of Fe(III) with HNPz was achieved by agitating aqueous solutions of Fe(III) with various concentrations of HNP_z in chloroform for 45 minutes.

Treatment of Rate Data

The mathematical treatment of the extraction data is as reported elsewhere.[3,5]

Extraction Equilibrium

The extraction equilibrium of Fe(III) with an acidic extractant, HNPz follows the following equilibrium relation:

$$Fe(III)_{aq} + 3HNPz_{(org)} \overset{K_{ex}}{\rightleftharpoons} Fe(NPz)_{3(org)} + 3H^{+}_{(aq)} \tag{1}$$

$$K_{ex} = \frac{[Fe(NPz)_3]_{org}\,[H^+]^3}{[Fe(III)]\,[HNP_z]^3_{org}} \tag{2}$$

But the ratio of $[Fe(NPz)_3]_{org}$ to [Fe(III)] is the distribution ratio, D. Therefore:

$$D = \frac{K_{ex}\,[HNPz]_{org}}{[H^+]} \tag{3}$$

and

$$logD = logK_{ex} + 3\,log\,[HNPz]_{org} + 3pH \tag{4}$$

The species without subscripts represent those in the aqueous phase. Equation (4) was used for calculating the extraction equilibrium constant, K_{ex} from the experimental data.

Rate of Backward Extraction

The rate of backward extraction of Fe(III) may be expressed by eqn. (5) as:

$$\frac{-d[Fe(NPz)_3]_{org}}{dt} = k_b\,[Fe(NPz)_3]^{p}_{org}\,[HNPz]^{q}_{org}\,[H^+]^{r} \tag{5}$$

where k_b is the rate constant for the backward extraction, and p,q and r are the respective reaction orders. When the extractant and H^+ ions are in excess relative to $Fe(NPz)_3$, the above equation may be represented as:

$$\frac{-d\,[Fe(NPz)_3]_{org}}{dt} = S^1\,[Fe(NPz)_3]^{p}_{org} \tag{6}$$

Where $S^1 = k_b\ (hl)^q_{org}\ (h)^r$; hl and h are the fixed extractant and H^+ ion concentrations respectively.

Therefore,

$$\frac{-d\,[Fe(NPz)_3]_{org}}{[Fe(NPz)_3]^p_{org}} = S^1 dt = k_b\,(hl)^q_{org}\,(h)^r \tag{7}$$

When the reaction order, p with respect to $[Fe(NPz)_3]_{org}$ is unity, as was the case in the present study, the following mathematical treatment is possible. If p = 1; then,

$$=\frac{dln\ [Fe(NPz)_3]_{org}}{dt} = S^1 \tag{8}$$

Integration of eqn. (8) gives:

$$-\log\,[Fe(NPz)_3]_{org} = S^* t + C \tag{9}$$

Where C is the integration constant, and S^* is equal to

$S^1/2.303$ (or $0.4342 \times S^1$).

By eqn. (9), a plot of $-\log[Fe(NPz)_3]_{org}$ vs. t should give a straight line with a slope equal to S^* ($0.4342 \times S^1$).

In order to obtain the reaction order with respect to $[HNPz]_{org}$ and $[H^+]$ in equation (5), measurements were made with one of these quantitites kept constant. Thus, by keeping H^+ ion concentration constant, various concentrations of HNPz are used. For a particular HNPz concentration, the extraction procedure is taken through the various time intervals. The slope, S^*_{HNPz} is obtained from the linear portion of the plot, and the corresponding parameter, S^1_{HNPz} calculated. Hence, when the H^+ ion concentration is fixed at h, the parameter, S^1_{HNPz} may be defined as:

$$\log S^1_{HNPz} = \log k_b (h)^r + q \log\,[HNPz]_{org} \tag{10}$$

From equation (10), the order of backward extraction, q, with respect to [HNPz]org can be obtained from the slope of the plot of $\log S^1_{HNPz}$ vs. $\log[HNPz]_{org}$. Similarly, when the concentration of HNPz is fixed at *hl*, then the parameter, $S^1_{H^+}$ is expressed as:

$$\log S^1_{H^+} = \log k_b (hl)^q + r \log\,[H^+] \tag{11}$$

and r can similarly be calculated.

RESULTS AND DISCUSSION

The experimental equilibrium data are given in Table 1. The results show that the distribution ratio, D is proportional to $[HNPz]^3_{org}$ and $[H^+]^{-3}$, indicating that Fe(III) exists as $Fe(NPz)_3$ in the organic phase. Experiments conducted to determine the degree of dependency of extraction on pH showed that D is third-power dependent on $[H^+]$, as a plot of log D vs. pH gave a straight line up to pH 2.5, with a slope of 3.

Table 1: Extraction equilibrium data

$[H^+] = 0.001 Mdm^{-3}$ (equation 3)

$\log [HNPz]_{org}$	logD	$\log K_{ex}$
- 2.70	0.10	- 0.80
- 2.50	0.70	- 0.80
- 2.40	0.95	- 0.85
- 2.30	1.30	- 0.80
- 2.25	1.60	- 0.65
- 2.00	2.35	- 0.65
- 1.80	2.65	- 0.68
	Av. $\log K_{ex}$ =	- 0.75
	and K_{ex} =	0.18

Rate of Extraction

The plot of $-\log [Fe(NPz)_3]_{org}$ vs t gave a straight line at the initial rate, indicating that the rate of backward extraction of iron is first order with respect to $[Fe(NPz)_3]_{org}$, i.e., p = 1. This is shown in Figure 1. The dependence of the rate of stripping iron on $[H^+]$ and $[HNPz]_{org}$ are respectively, shown in Figures 2 and 3, as plots of $\log S^1_{H^+}$ vs. $-\log [H^+]$ and $\log S^1_{HNPz}$ vs. $\log [HNPz]_{org}$ with slops of -1.08 and -1.0. The substitution of these values into equations. (10) and (11) demonstrates a first order dependence on $[H^+]$ i.e. r = 1.0 and inverse first order dependence on [HNPz]org , i.e. q = -1.0 of the backward extraction of iron(III).

From the above results, the equation for the rate of backward extraction of iron(III) can thus be re-written as:

$$\frac{-d\,[Fe(NPz)_3]_{org}}{dt} = \frac{k_b\,[(NPz)_3]_{org}\,[H^+]}{[HNPz]_{org}} \qquad (12)$$

From the foregoing, therefore, the backward extraction of iron on the overall, is a first order process. Applying the results, and using equation (5), the velocity constant, k_b was calculated as $2.7 \times 10^3 s^{-1}$.

In the kinetic studies of the rate of extraction of Fe(III) using thenoyltrifluoroacetone (HTTA), Sekine *et al.*[11,12] established the rate-determining step as the reaction between the undissociated HTTA and Fe(III) at higher acid concentrations. On the other hand, Mirza *et al.*[5] in their kinetic studies of the rate of forward extraction of zirconium ions from aqueous sulphate medium using 4-benyzoyl-3methyl-1-phenyl-5-pyrazolone (HPz) in chloroform and backward extraction of the zirconium pyrazolonate chelate from the organic phase, has reported the rate-determining step for the forward extraction to be the formation of the second complex between the anion, Pz^- and the aquated species, $Zr(H_2O)_2SO_4Pz^+$ in the aqueous phase.

In the present study, the nature of iron species that are involved in the rate-determining step is not certain. But in simple terms, the equilibrium steps involved in the backward extraction of iron from the organic phase may by represented by the following:

$$Fe(NPz)_{3(org)} \rightleftharpoons Fe(NPz)_{3(aq)} \tag{13}$$

$$Fe(NPz)_{3(aq)} \rightleftharpoons Fe(NPz)_2^+ + Npz \tag{14}$$

$$Fe(NPz)_2^+ \rightleftharpoons Fe(NPz)^{2+} + NPz^- \tag{15}$$

$$Fe(NPz)^{2+} \rightleftharpoons Fe^{3+} + Npz^- \tag{16}$$

$$Npz^- + H^+ \rightleftharpoons HNPz_{(aq)} \tag{17}$$

$$HNPz_{(aq)} \rightleftharpoons HNPz_{(org)} \tag{18}$$

Step 4, equation (16) is proposed to be the rate-determining step, i.e., the dissociation of $Fe(NPz)^{2+}_{aq}$ to Fe^{3+} and NPz^-. In other words, the rate is controlled by the ability or otherwise of Fe^{3+} to recombine with NPz^- to form $Fe(NPz)^{2+}$. However, the rate-determining step may not be as straight forward as suggested. It may involve some complicated derivatives.

The mechanism of back extraction may, however, be more complex than is simplified by the above equations. Various aquo and hydroxo complexes of Fe(III) have been proposed [13,14] to exist in dilute acid solution, *viz.* $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5OH^{2+}$ etc. Therefore, the consecutive steps shown in equations (13) to (18) may involve, among others, ligand exchange, in which the pyrazolonato anions, NPz^- are consecutively eliminated by water molecules and/or hydroxy ions.

It is, therefore, reasonable to assume at this point that the transfer of the pyrazolonate chelate from the bulk organic phase to the acid solution is an important process, which is followed by rapid successive exchange of pyrazolonate anions by aqueous solvent molecules to give the overall equilibrium raction, e.g.

$$Fe(NPz)_{3(org)} + 6H_2O \overset{3H^+}{\rightleftharpoons} Fe(H_2O)^{3+}_{6(aq)} + 3HNPz_{(org)}$$

CONCLUSION

The rate of stripping iron(III) with aqueous solution has been noted to be highly affected by hydrogen ion concentration. The rate increased as $[H^+]$ is increased. The mechanism of back extraction is proposed to be the successive exchange of the extractant anions by the solvent molecules/ions to form aquo and hydroxy complexes of Fe(III); while the rate-controlling step involves the dissociation of the iron(III) monopyrazolonato chelate to Fe^{3+} and NP_z^-, followed by fast protonation of the NP_z^- anion, and rapid transference of same to the organic phase.

Acknowledgement

The authors are grateful to Abia State University, Uturu for sponsoring M.O.C.

References

1. Eigen M. (1963). Rate of extraction of metal ions from aqueous solutions. *Pure and Applied Chemistry* **46**: 38.

2. Bolomy R.A. & Wish L. (1950). *Journal of the American Chemical Society* **72**: 4486-4489.

3. Sekine T., Koibe Y. & Komatsu Y. (1971). Rate of extraction of Fe(III) from aqueous solution using Tri-n-butylphosphate. *Bulletin Chemical Society of Japan* **32**: 2907-2910.

4. McClellan B. E. & Fraiser H. (1964). Kinetic Studies of Zn(II) with di-α-naphthylthiocarbazone in choloroform. *Analytical Chemistry* **36**: 2262-2265.

5. Mirza M. Y., Nwabue F.I. & Okafor E.N. (1981). Kinetic studies of the solvent extraction of metal complexes - I. The rate of extraction and back-extraction of Zr(VI) 1-phyenyl-3-methyl-4-benzoyl-pyrazolonate chelate. *Journal of Inorganic and Nuclear Chemistry* **43**: 1363-1369.

6. Fleming C.A. & Nicol M.J. (1980). Kinetic studies of solvent extraction of Fe(III) using 8-hydroxyquinoline dissolved in chloroform. *Journal of Inorganic and Nuclear Chemistry* **42**: 1327-1330.

7. Fleming C.A. & Nicol M.J. (1980). Kinetic studies of solvent extraction Cu(II) using 8-hydroxyquinoline dissolved in chloroform. *Journal of Inorganic and Nuclear Chemistry* **42**: 1335-1337.

8. Jensen B.S. (1959). *Acta Chimica Scandinavia* **13**: 1668.

9. Okafor E.C. (1980). Structures of 1-phenyl-3-methyl-pyrazolone and its Derivatives (NMR, Mass & IR spectra). *Zhurnal Naturforschung* **85b**: 1019-1023.

10. Jayan T.C.Z., Subramanian S. & Wijedesa M.A. (1975). *Analyst* **100**: 716.

11. Sekine T., Komatsu Y. & Yumikura Y. (1973). Kinetic studies on the solvent extraction of Fe(III) with thenoyltrifluoroacetone. *Bulletin of the Chemical Society of Japan* **46**: 3897-3900.

12. Sekine T., Komatsu Y. & Yumikura Y. (1973). Kinetic studies on the solvent extraction of Ga(III) with thenoyltrifluoroacetone. *Journal of Inorganic and Nuclear Chemistry* **35**: 3897-3899.

13. Burgess J. (1978). *Metals in Solutions.* pp. 24. Ellis Horwood, Chichester.

14. Lee D.J. (1975). *A Concise Inorganic Chemistry.* (3rd ed); pp. 354. Van Nostrand.