

Original Article

Kinetics and Mechanism of Solvent Extraction of Manganese(II), Lanthanum(III) and Zirconium(III) from Aqueous Solution with Chloroform Solution of 3-Methyl-1-Phenyl-4-Stearoylpyrazol-5-One

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Abstract - Kinetics and mechanism of solvent extraction of manganese(II), lanthanum(III), and zirconium(III) in their aqueous solutions with chloroform solution of 3-methyl-1-phenyl-4-stearoylpyrazol-5-one (HSPy) have been investigated at various conditions of pH and HSPy concentrations. Experimental observation shows that the rate is first order with rate law: $-d[M^{n+}]/dt = k_f[M^{n+}][SPy]$; and is proportional to $[M^{n+}]$, $[HSPy]$ and $[H^+]^{-1}$; where $M^{n+} = Mn^{2+}$, La^{3+} and Zr^{3+} . The rate constants, k_f were determined to be 0.8324 min^{-1} for Mn^{2+} , 0.9977 min^{-1} for La^{3+} and 0.9971 min^{-1} for Zr^{3+} ; the order of rates of extraction for the metals being $La^{3+} > Zr^{3+} > Mn^{2+}$. This suggests that the rates increase with larger size and higher ionic charges. The mechanism was proposed in which the rate-determining step is the formation of the first chelate ring of the mono-pyrazolonato metal complex; $[Mn(H_2O)_4(SP_y)]^+$; $[La(H_2O)_4SP_y]^{2+}$ and $[Zr(H_2O)_4SP_y]^{2+}$.

Keywords - Kinetics, Mechanism, Solvent extraction, Acylpyrazolones, Formation constant, Metals.

I. INTRODUCTION

Extraction and reuse of metal ions are of immense significance, especially when the supply is restricted [1]. The extraction of metals through the process of solvent extraction is a key step in many hydrometallurgical processes. Solvent extraction studies of certain metals have been undertaken by various workers [2], [3], using β -diketones, especially 4-acyl derivatives of 1-phenyl-3-methyl pyrazolone, which are

known to have several advantages over open-chain β -diketones like

2-thenoyltrifluoroacetone (HTTA) and its derivatives. For instance, the metal chelate complexes of the 1-phenyl-3-methylpyrazolone have high extracting ability; the complex extracts have intense colors; again, they are highly soluble in most organic solvents and form highly stable neutral metal complexes that are principally hydrophobic [4].

Moreover, the formation of the metal complexes with acylpyrazolones is applied for the separation of elements with similar properties, i.e., lanthanides, coinage metals, actinides, early transition metals, etc. [5]. 4-acylpyrazol-5-ones, as modified β -diketones are able to extract metal ions at lower pH values than open-chain β -diketones [6]. Therefore, they offer the possibility of avoiding the pH region where hydrolysis of the metal ions takes place.

Again, the peripheral positions 1, 3, and 4 in the pyrazolone can be easily changed with different alkyl and other groups in order to vary the electronic and steric features of the acylpyrazolone ligands. The 4-benzoyl derivative of 1-phenyl-3-methylpyrazolone has received much attention in the selective extraction of metal ions from acid solutions [7].

In order to understand the factors that determine selectivity during solvent extraction, the rate and mechanism of the recovery of three metal ions have been examined. The rate of recovery of metal ions from aqueous solution has been postulated to be slow when the charge is large and/ or the radius is small. This has been attributed to the slow substitution of the coordinated water molecules on the metal [8].



The present study was carried out to measure the rate of recovery of manganese(II), lanthanum(III), and zirconium(III) from their aqueous solutions with chloroform solution of 3-methyl-1-phenyl-4-stearoylpyrazol-5-one and to determine the mechanism that may be involved in the reaction process.

II. EXPERIMENTAL METHODS

A. Reagents

Analytical grade reagents including ethyl acetoacetate, phenylhydrazine, stearoyl chloride, 95% ethanol, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in their pure forms. Distilled de-mineralized water was also used.

B. Syntheses of the ligand (HSPy)

The ligand, 3-methyl-1-phenyl-4-stearoylpyrazol-5-one (HSPy), was synthesized and characterized according to the procedures outlined in the literature [9], [10], [11], [12], [13], and [14].

C. Extraction procedure and rate of recovery of the metals

a) Effect of concentration of the ligands on the solvent extraction

Studies on the solvent extraction of the three metals were carried out by agitating 5 cm³ of the various aqueous solutions containing 0.025 M $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 0.017 M of $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, and 0.017 M of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ at buffer 4 with various concentrations of HSPy (0.01 – 0.2 molar) for 30 min at 26°C ± 0.5°C in a separating funnel, using a rotary shaker (Maxi Mix III, Thermo Scientific, Type 65800 model). The pH value of the buffer was measured using a digital pH meter Model pHs-25 which was standardized with three buffer solutions of pH 4, 7, and 9 prior to the pH measurement [15].

Preliminary experiments showed that optimum extractions were obtained at pH 4; and that 25 to 30 min was sufficient for equilibration.

The two phases were allowed to separate at each extraction process, and the concentrations of the Mn(II), La(III), and Zr(III) remaining in the aqueous phase were determined spectrophotometrically, using a 2500 PC model Uv-visible spectrophotometer at wavelengths of 279.5 nm, 360.1 nm, and 550.1 nm respectively, being the wavelengths of maximum absorption (λ_{max}) for each metal. Standard solutions of the metals were prepared and diluted to get lower concentrations. Their absorbance, together with those of the test solutions, was measured at the specified wavelengths, as listed above for each of the metals. Various absorbance readings were obtained for the various concentrations, and a graph of absorbance against metal concentrations was plotted to determine the concentrations of the metals remaining in the aqueous phase. The metal extracted into the organic phase in each case, therefore, was found by the difference in mass (initial mass before

extraction minus mass after extraction with the HSPy) [16], [15], [17], and [8].

b) Effect of pH medium on the solvent extraction

Studies on the dependence of extraction on the pH of the aqueous solutions of the three metal ions were carried out; again, by agitating 5 cm³ of the same standard solutions of Mn(II), La(III), and Zr(III) ions at various pH values of 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.2, 3.5, 4.0, 4.5 and 5.0, with 5 cm³ of 0.02 M solution of HSPy in chloroform for equilibration time of 30 minutes at 26°C ± 0.5°C using a rotary shaker, Maxi Mix III, Thermo Scientific, Type 65800 model. Buffer solutions ranging from pH 0 to 5 were used [7]. The pH values were measured with a digital pH meter Model pHs-25. Two phases were obtained, separated, and the different masses extracted were determined, as in (A) above.

D. Rate of recovery of the metal

Studies on the rate of recovery of the three metals were carried out by agitating 5 cm³ of acidified standard solutions of the Mn(II), La(III), and Zr(III) at pH 4, with 5 cm³ of 1.0 M solution of HSPy in chloroform for resident times ranging from 10 to 60 min in a separating funnel. A rotary shaker (Maxi Mix III, Thermo Scientific Type 65800) was used.

The phases were separated at each extraction process, and the concentrations of the Mn(II), La(III), and Zr(III) remaining in the aqueous phase were determined spectrophotometrically.

III. RESULTS AND DISCUSSION

The rate of recovery of the metal ions from the aqueous phase was followed as the rate of disappearance of the metal ions, M^{n+} from the aqueous phase during the solvent extraction, and is represented by the following expressions:

$$-d[\text{M}^{n+}]/dt = k_f[\text{M}^{n+}]^a[\text{HSPy}_{(\text{org})}]^b[\text{H}^+]^c; \quad (1);$$

where; $-d[\text{M}^{n+}]/dt$ is the rate of recovery of the metal ions; k_f is the rate constant for the recovery process; $[\text{M}^{n+}]$ is the molar concentration of the metal ions; $[\text{HSPy}_{(\text{org})}]$ = molar concentration of the extractant, HSPy; $[\text{H}^+]$ = hydrogen ion concentration; related to pH of the metallic ion aqueous solutions; while a, b and c are the stoichiometries or reaction orders as appropriate.

When $[\text{HSPy}_{(\text{org})}]$ and $[\text{H}^+]$ are present in excess, equation (1) becomes:

$$-d[\text{M}^{n+}]/dt = k_1[\text{M}^{n+}]^a \quad (2)$$

Substitution of the data in Table (1) into the rate law expression for a first-order reaction;

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$$

(a = initial concentration; a-x = concentration at any given time, t) gave relatively constant values of k_1 , showing that

equation (2) is first order, hence the superscript, $a=1$. Therefore integration of equation (2) will give:

$$-\log[M^{n+}] = k_1 t + C \quad (3);$$

where; C is a constant and;

$$k_1 = k_f [HSPy_{(org)}]^b \cdot [H^+]^c \quad (4)$$

Table (1) gives the relevant data for the plot of equation (3) shown in Figure (1) for the different metals extracted. Linear plots were obtained to further confirm the first-order nature of the extraction process [18], [19].

To obtain the reaction orders; b and c, measurements are made with one of the quantities $[HSPy_{(org)}]$ or $[H^+]$ kept fixed while the other is varied. Thus, when $[H^+]$ is kept constant, the logarithm of equation (4) becomes:

$$\log k_{1(HBPY)} = \log k_f [H^+]^c + b \cdot \log [HSPy_{(org)}]; \quad (5)$$

from which b can be determined.

Similarly, when $[HSPy_{(org)}]$ is kept constant, equation (4) becomes:

$$\log k_{1H^+} = \log k_f [HSPy]^b + c \cdot \log [H^+]; \quad \text{OR}$$

$$-\log k_{1H^+} = -\log k_f [HSPy]^b + pH; \quad (6)$$

from which c can be determined from the slope of a plot of $\log k_{1(H^+)}$ against $\log [H^+]$ or; $-\log k_{1(H^+)}$ versus pH.

The rate constant for the recovery process, k_f , can then be calculated from the intercept of plots of equation (5) or (6) when values of a, b and c are known [8].

Table (2) gives the relevant data for the plot of equation (5) shown in Figure 2, while Table 3 gives the relevant data for the plot of equation (6) shown in Figure 3 for the different metals extracted.

A plot of $\log k_{1(HSPY)}$ versus $\log [HSPy_{(org)}]$ in Figure 2 for the metal ions gave linear plots and had slopes, b of: 0.53(Mn), 0.83(La), and 0.90(Zr).

Similar plots of $-\log k_{1(pH)}$ versus pH in Figure 3 for each of the metal ions are also linear with negative slopes, c, of -0.30(Mn), -0.73(La), and -0.71(Zr).

These results show that the rate of recovery of the metal ions from an aqueous solution with HSPy depends on the metal ions and ligand concentrations; and the inverse of hydrogen ion concentrations of the aqueous metal ion solutions. The same observation had been reported elsewhere [4], [5], [8].

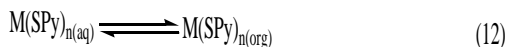
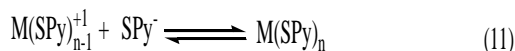
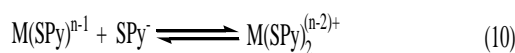
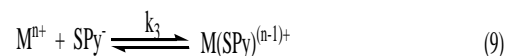
The values of the rate constants, k_f for the forward reactions, therefore were determined from the intercepts of Figure 2 (-1.26, -0.92 and -0.88, for Mn, La, and Zr respectively); and are found to be 0.8324 min^{-1} for Mn, 0.9977 min^{-1} for La, and 0.9971 min^{-1} for Zr.

From the determined results, it is observed that the order of rates of extraction for the metals is: $La^{3+} > Zr^{3+} > Mn^{2+}$. This shows that the rates of solvent extraction of the metals increase with larger size and higher ionic charges. This suggests that the rate depends on the ionic charge. Hence the greater the charge on the ion, the greater the effective nuclear charge (Z_{eff}), leading to greater attraction of the orbitals of the ligands, hence faster reaction rates.

Again, the observed trend depicts a decrease in the number of vacant d-orbitals of the metal ions investigated. For instance; the La^{3+} (with electronic configuration $[Xe]5d^0$) and Zr^{3+} (with $[Kr]4d^1$ electronic configuration) have five and four vacant d-orbitals, respectively, which could be used to accommodate more lone pairs of electrons of the HSPy ligand faster than the Mn^{2+} (electronic configuration $[Ar]3d^5$) with no vacant d-orbitals; hence the formation of faster-coordinated intermediates probably through associative or substitution nucleophilic bimolecular (S_N2) mechanism by the La^{3+} and Zr^{3+} . A similar report had been recorded elsewhere [20], [21].

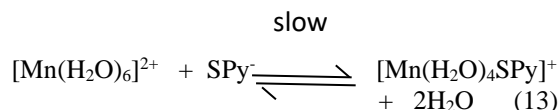
A. Mechanism of the solvent extraction reaction

The steps involved in the extraction of the metal ions from the aqueous phase into the organic phase are as follows [8]:

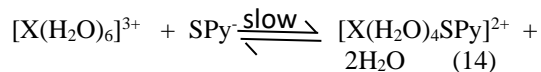


Since equations (7) and (12) do not involve a pH-dependent process, they cannot be considered as rate-determining steps. Equation (8) can also be eliminated on the grounds that it does not show first-order dependence on the metal ion. Equations (10) and (11) are eliminated on the grounds that they show dependence on the square or more of ligand concentration. That leaves equation (9) which is first order in both the metal ion and ligand concentration. Equation (9), therefore, represents the rate-determining step of the extraction process.

Considering that the metal ions are hydrated in an aqueous solution; therefore, the rate-determining step or equation (9) can be rewritten specifically as follows:



and;



where; X = La or Zr.

Thus, the formation of the first chelate ring of the mono-pyrazolonato metal complex is the rate-determining step. This step probably involves a slow bond-weakening effect exerted by the bidentate HSPy on the two water molecules, which are probably *trans* to each other (*Trans Effect*), leading to their elimination. The other steps are expected to follow in quick succession leading to neutral bis-pyrazolonato complexes of Mn(II) and tris-pyrazolonato complexes of La(III) and Zr(III), which are transferred into the organic phase [22].

From equation (9) therefore; rate = $k_3[\text{M}^{n+}][\text{SPy}^-]$ (15)

Since SPy^- is an intermediate, not a reactant, $[\text{SPy}^-]$ has to be expressed in terms of the concentration of reactants. To do this, we use the steady-state approximation (SSA) [23].

Following the steady state approximation (SSA) and taking recourse of equations (8) and (9), it is deduced that:

$$\begin{aligned} \text{rate of producing } \text{SPy}^- &= k_1[\text{HSPy}]; \\ \text{rate of consuming } \text{SPy}^- &= k_2[\text{H}^+][\text{SPy}^-] + \\ &\quad k_3[\text{M}^{n+}][\text{SPy}^-] \end{aligned}$$

producing rate of SPy^- = consuming rate of SPy^- ; therefore:

$$k_1[\text{HSPy}] = k_2[\text{H}^+][\text{SPy}^-] + k_3[\text{M}^{n+}][\text{SPy}^-] \quad (16)$$

$$[\text{SPy}^-] = \frac{k_1[\text{HSPy}]}{k_2[\text{H}^+] + k_3[\text{M}^{n+}]} \quad (17)$$

Substituting equation (17) into the rate expression, equation (15) gives:

$$\text{rate} = k_3[\text{M}^{n+}] \cdot \frac{k_1[\text{HSPy}]}{k_2[\text{H}^+] + k_3[\text{M}^{n+}]} \quad (18)$$

$$\text{rate} = \frac{k_1 k_3 [\text{M}^{n+}] [\text{HSPy}]}{k_2 [\text{H}^+] + k_3 [\text{M}^{n+}]} \quad (19)$$

Since equation (9) is slow, then; k_3 and $k_2 \gg k_3[\text{M}^{n+}]$; and equation (8);

$[\text{HSPy}] = [\text{H}^+] + [\text{SPy}^-]$, the rate law is deduced to:

$$\text{rate} = \frac{k_1 k_3 [\text{M}^{n+}] [\text{SPy}^-]}{k_2} \quad (20)$$

$$\text{rate} = k[\text{M}^{n+}][\text{SPy}^-]. \quad (21)$$

$$\text{where; } k = \frac{k_1 k_3}{k_2} \quad (22)$$

Since the rate law, equation (21) is first order with respect to both reactants and similar to equation (15), it can be concluded that the rate law also supports the proposed mechanism.

Table 1: Data on the extent of extraction of the metal ions for one hour at intervals of 10 min using HSPy ligand at an initial concentration of $\text{M}^{n+} = 0.50$

T(min)	$\text{Mn}(\text{SPy})_2$		$\text{La}(\text{SPy})_3$		$\text{Zr}(\text{SPy})_3$	
	$[\text{Mn}^{2+}]$	$-\log [\text{Mn}^{2+}]$	$[\text{La}^{3+}]$	$-\log [\text{La}^{3+}]$	$[\text{Zr}^{3+}]$	$-\log [\text{Zr}^{3+}]$
10	0.41	0.39	0.40	0.40	0.44	0.36
20	0.35	0.46	0.36	0.44	0.35	0.46
30	0.28	0.55	0.33	0.48	0.32	0.49
40	0.20	0.70	0.30	0.52	0.23	0.64
50	0.13	0.89	0.26	0.59	0.16	0.80
60	0.11	0.96	0.25	0.60	0.15	0.82

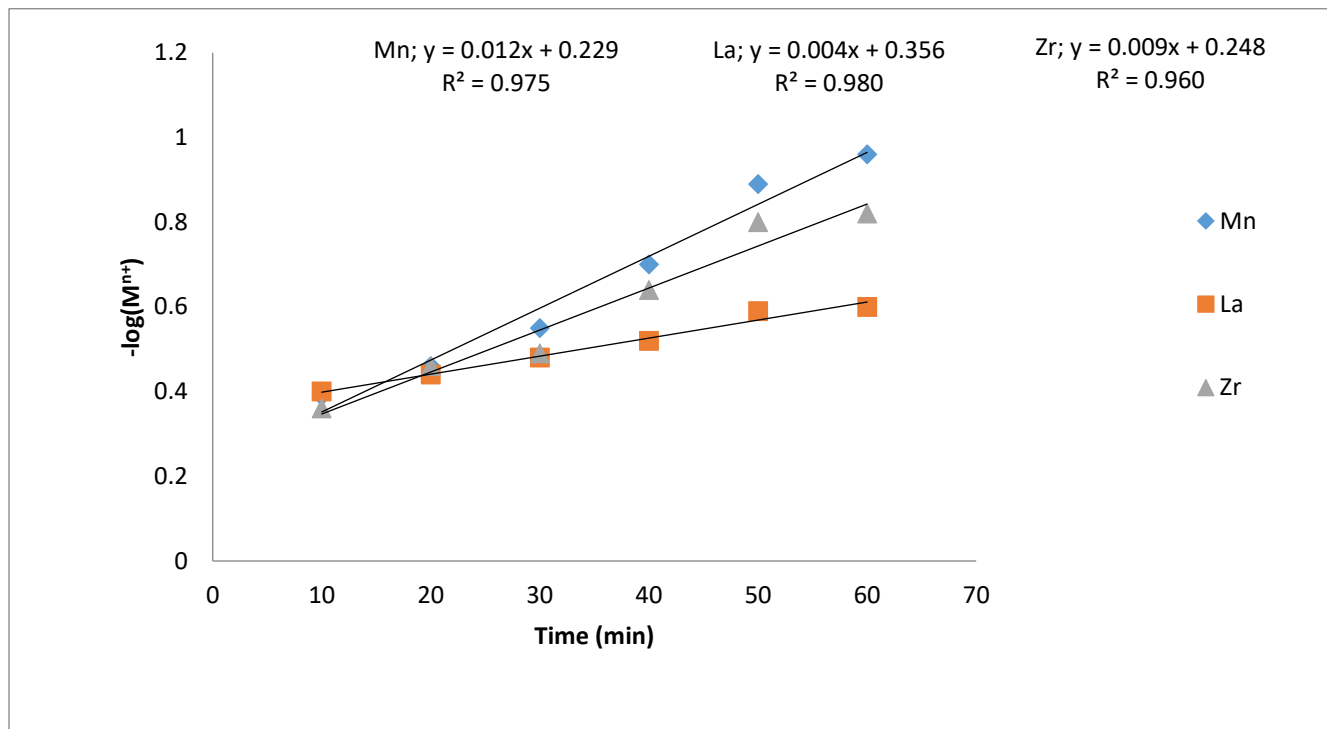


Figure 1: Plot of data on the extent of extraction of the metal ions for one hour at intervals of 10 min using the HSPy ligand

Table 2: Rate of extraction of the metal ions at different concentrations of the HSPy ligand at pH 4 for 30 min

		Mn(SPy) ₂ .2H ₂ O		La(SPy) ₃ .2H ₂ O		Zr(SPy) ₃ .2H ₂ O	
[HSPy]	Log[HSPy]	Rate (k)	Log k	Rate (k)	Log k	k	Log k
0.01	-2.00	0.0030	-2.52	0.0007	-3.15	0.0007	- 3.15
0.02	-1.70	0.0073	-2.14	0.0083	-2.08	0.0073	-2.13
0.03	-1.52	0.0100	-2.00	0.0113	-1.95	0.0060	-2.22
0.04	-1.40	0.0127	-1.90	0.0117	-1.93	0.0090	-2.05
0.05	-1.30	0.0143	-1.84	0.0143	-1.84	0.0137	-1.86
0.06	-1.22	0.0147	-1.83	0.0153	-1.81	0.0140	-1.85
0.07	-1.15	0.0153	-1.81	0.0158	-1.80	0.0147	-1.83
0.08	-1.10	0.0155	-1.81	0.0161	-1.79	0.0153	-1.81
0.09	-1.05	0.0157	-1.80	0.0162	-1.79	0.0157	-1.80
0.10	-1.00	0.0159	-1.80	0.0164	-1.79	0.0162	-1.79
0.15	-0.82	0.0163	-1.79	0.0166	-1.78	0.0165	-1.78
0.20	-0.70	0.0165	-1.78	0.0166	-1.78	0.0166	-1.78

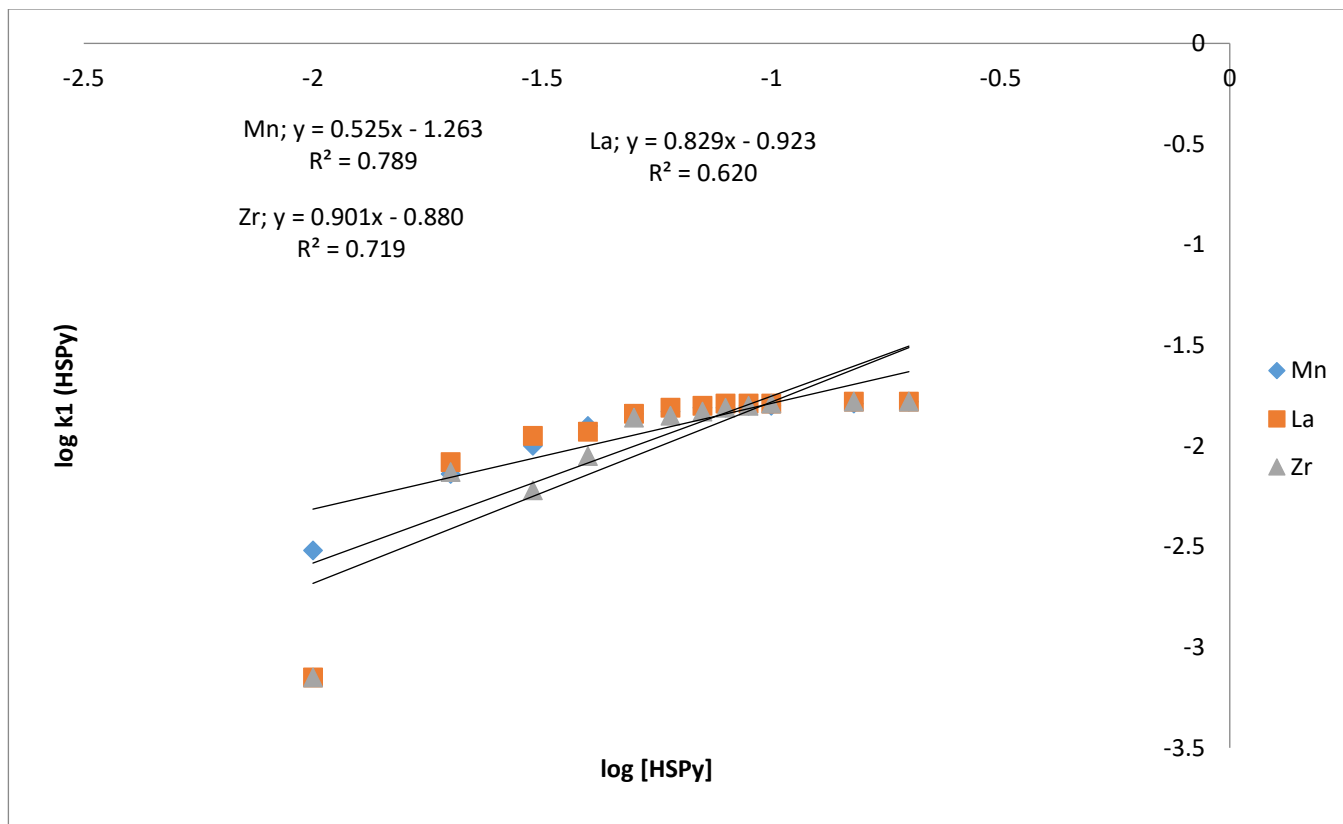


Figure 2: Plot of data on the rate of solvent extraction of the metal ions at different HSPy concentrations

Table 3: Rate of solvent extraction of the metal ions at different pH of the aqueous solutions of the metal ions at 0.02 M of HSPy for 30 min

pH	Mn(SP _y) ₂		La(SP _y) ₃		Zr(SP _y) ₃	
	Rate(k)	-Log k	k	-Log k	k	-Log k
0.0	0.0010	3.00	3.3 x 10 ⁻⁵	4.48	3.3 x 10 ⁻⁵	4.48
1.0	0.0013	2.89	6.7 x 10 ⁻⁵	4.18	6.7 x 10 ⁻⁵	4.18
2.0	0.0020	2.70	3.3 x 10 ⁻⁴	3.48	0.0010	3.00
2.5	0.0073	2.13	0.0033	2.48	0.0147	1.83
3.0	0.0153	1.81	0.0153	1.81	0.0163	1.79
3.2	0.0163	1.79	0.0162	1.79	0.0167	1.78
3.5	0.0164	1.78	0.0167	1.78	0.0167	1.78
4.0	0.0166	1.78	0.0167	1.78	0.0167	1.78
4.5	0.0166	1.78	0.0166	1.78	0.0166	1.78
5.0	0.0166	1.78	----	---	---	---

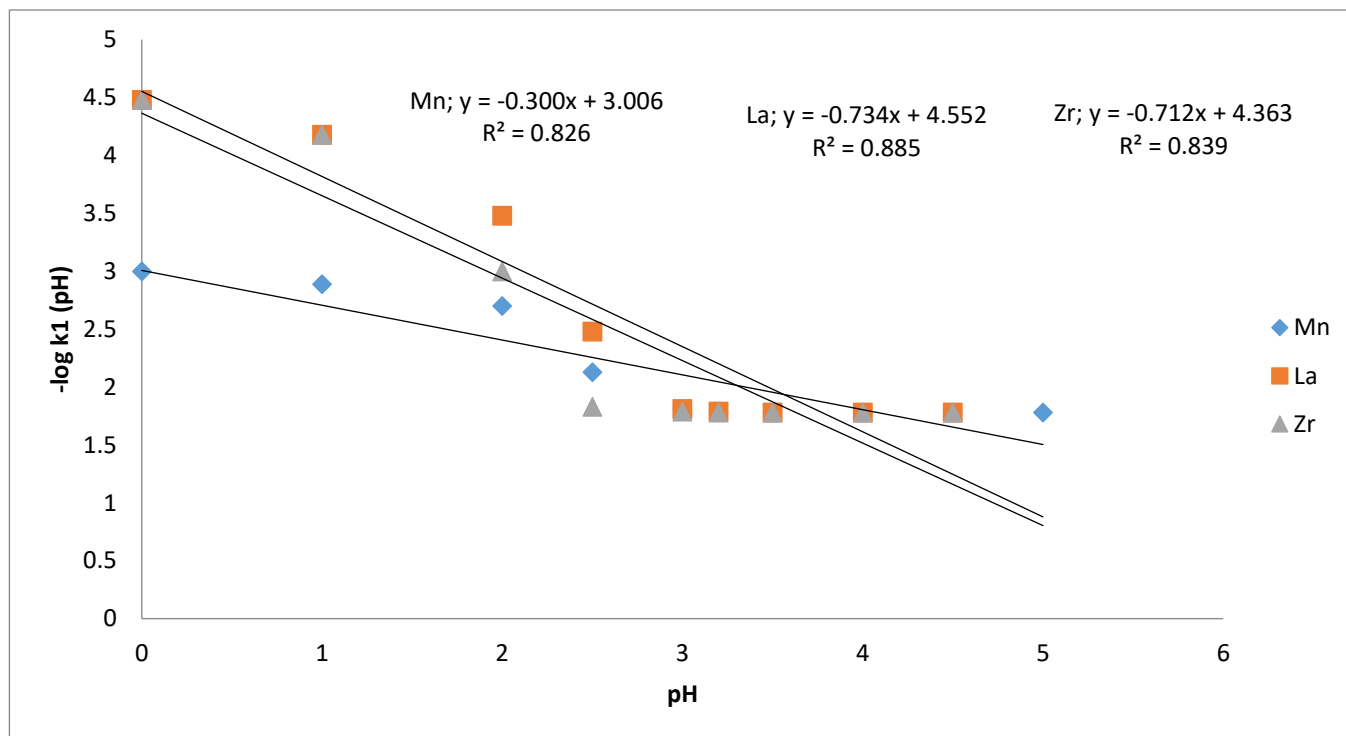


Figure 3: Plots of data on the rate of solvent extraction of Mn^{2+} , La^{3+} and Zr^{3+} ions at different pH values and 0.02 MHSPy concentration

IV. CONCLUSION

This study was undertaken to investigate the kinetics of solvent extraction of manganese(II), lanthanum(III), and zirconium(III) by chloroform solution of 3-methyl-1-phenyl-4-stearoylpyrazol-5-one, and a reaction mechanism has been proposed. The rate law is determined as:

$$-d[M^{n+}]/dt = k[M^{n+}][SPy].$$

The formation of the first chelate ring of mono-pyrazolonato metal complex and increase of rate constants with increasing metal and ligand concentrations is in accord with the proposed mechanism of the reaction.

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