



Solvent Extraction Studies of Lanthanum(III) and Vanadium(V) from Their Aqueous Solutions With Chloroform Solution of 1-Phenyl-3-Methyl-4-Butanoylpyrazol-5-One.

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ABSTRACT

Solvent extraction of lanthanum(III) and vanadium(V) from their aqueous solutions with chloroform solution of 1-phenyl-3-methyl-4-butanoylpyrazol-5-one (the ligand) was studied. The effects of ligand (extractant) concentrations and the pH of the metal aqueous solutions on the solvent extraction were evaluated in terms of their distribution coefficients (D) and the equilibrium constants (K_{ex}) were determined. The values of the slopes of the plots of $\log D$ versus $\log [HBP_{y(org)}]$ and that of $\log D$ versus pH showed that approximately 3 moles of the HBP_y ligand reacted with one mole of La^{3+} while 2 moles of the same ligand reacted with VO_2^+ during the extraction process. The average logarithms of the equilibrium constant (K_{ex}) values obtained for the metals at the different HBP_y concentrations and buffer 4 are -7.40 (La) and -5.14 (V); while those obtained at the different pH and a constant extractant concentration of 0.02 M are $La(BPy)_3 = -0.49$; and $VO_2(BPy)_2 = -1.39$; showing that the ligand is an efficient extractant for V(V) and La(III) ions from their aqueous solutions. The study has shown that separation of the La(III) and V(V) ions in their mixture is possible by the adjustment of the extractant concentrations and the pH of the aqueous solution of such mixture.

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Introduction

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, using β -diketones, especially 4-acyl derivatives of 1-phenyl-3-methylpyrazolone which are known to have several advantages over 2-theonyltrifluoroacetone (HTTA) and its derivatives^{1, 2}. For instance, the metal chelate complexes of the 1-phenyl-3-methyl-4-acylpyrazolone have high extracting ability; the complex extracts have intense colours; again, they are highly soluble in most organic solvents and form highly stable neutral metal complexes that are principally hydrophobic; 4-acylpyrazol-5-ones, as modified β -diketones, are able to extract metal ions at lower pH values than open-chain β -diketones³. 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 pyrazolones can be easily changed with different alkyl and other groups in order to vary the electronic and steric features of the acylpyrazolone ligands. Different factors affect the selectivity of particular metal ions during solvent extraction. Such factors include the nature of the ligands and the concentrations of the ligands, pH of the aqueous solution of the metal ions, duration of the extraction process, use of masking agents, etc.

The 4-benzoyl derivative of 1-phenyl-3-methylpyrazolone has received much attention in the selective extraction of metal ions from acid solutions⁴. This is to the detriment of the other derivatives.

The present study therefore was carried out to study the solvent extraction of La(III) and V(V) from their aqueous solutions using chloroform solution of 1-phenyl-3-methyl-4-butanoyl pyrazol-5-one (HBP_y); to determine the equilibrium constants of the solvent extraction process of the metal ions and the possibility of the use of the 1-phenyl-3-methyl-4-butanoyl pyrazol-5-one (HBP_y) in separating the La(III) and V(V) metal ions.

The structure of the ligand/ extractant, 1-phenyl-3-methyl-4-butanoylpyrazol-5-one (designated here as HBP_y) is as shown in Figure 1.

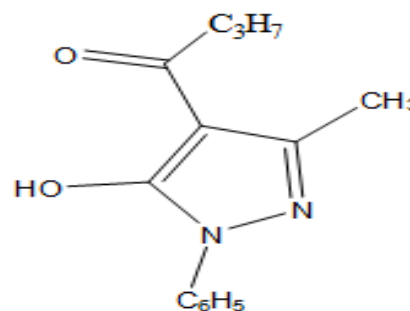


Figure 1. Structure of the 1-phenyl-3-methyl-4-butanoyl pyrazol-5-one (HBP_y), the extractant/ ligand.

2.0. Experimental

2.1. Preparations of the ligand and the metal aqueous solutions

The HBP_y was prepared from high grade butanoyl chloride and 1-phenyl-3-methylpyrazol-5-one which was prepared from analytical grade ethylacetate and phenylhydrazine^{5, 6}.

The HBPpy was recrystallized from aqueous ethanol (1:1), filtered, air-dried and stored over silica gel in a desiccator. It was dissolved in chloroform to obtain the desired concentrations⁷.

The stock solutions of La(III) and V(V) were prepared by dissolving 1.24 g (0.017 M) $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ and 0.30 g (0.025 M) NH_4VO_3 ; with distilled water in a beaker, transferred to a 100 ml volumetric flask; and made up to the mark with distilled water. Further dilutions were made by adding appropriate amounts of distilled water.

2.2. Extraction Procedure

Studies on the solvent extraction of the two metals were carried out by agitating 5 ml of the aqueous solution containing 5 mg/l of the V(V) and La(III) with 5 ml of the various concentrations of HBPpy (0.01 – 0.2 M) for 30 minutes at $26^\circ\text{C} \pm 0.5^\circ\text{C}$ in a separating funnel, using a rotary shaker¹⁰.

The study was also carried out by agitating the same 5 ml of the V(V) and La(III) solutions at various pH values of 0 to 5 for a specific time of 30 minutes with 5 ml of 0.2 M solution of HBPpy in chloroform using a rotary shaker. For the pH studies, the aqueous solutions of the metallic ions were adjusted to different pH values using HCl and Na_2CO_3 to cover pH 0 to 5⁸. The pH values were measured with 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.

The phases were separated at each extraction process and the concentrations of the V(V) and La(III) remaining in the aqueous phase were determined spectrophotometrically using a Uv-visible 2500 PC model spectrophotometer at wavelengths of 318.4 nm and 550.1 nm for the V(V) and La(III) respectively being the wavelengths of maximum absorption (λ_{max}) for each metal. The metal extracted into the organic phase in each case was found by the difference in mass⁷.

2.3. Extraction Equilibrium

The extraction of the metal ions (M^{n+}) from an aqueous phase using the ligand (HBPpy) in the organic phase can be treated as follows:



where K_{ex} is the extraction equilibrium constant;

$$K_{\text{ex}} = \frac{[\text{M}(\text{BPy})_{n(\text{org})}] \cdot [\text{H}^+]^n}{[\text{M}^{n+}] \cdot [\text{HBPpy}_{(\text{org})}]^n} \quad (2)$$

The Distribution ratio, D, which is the ratio of the concentration of the metal into the organic phase to that in the aqueous phase, is given as:

$$D = \frac{[\text{M}(\text{BPy})_{n(\text{org})}]}{[\text{M}^{n+}]} \quad (3)$$

Substitution of D in equation (3) into equation (2) gives:

$$K_{\text{ex}} = D \cdot [\text{H}^+]^n / [\text{HBPpy}_{(\text{org})}]^n \quad (4)$$

$$D = K_{\text{ex}} \cdot [\text{HBPpy}_{(\text{org})}]^n / [\text{H}^+]^n \quad (5)$$

Taking the logarithms of both sides of equation (5) gives:

$$\text{Log } D = \text{Log } K_{\text{ex}} + n \log[\text{HBPpy}_{(\text{org})}] - n \log[\text{H}^+] \quad (6)$$

Or

$$\text{Log } D = \text{Log } K_{\text{ex}} + n \log[\text{HBPpy}_{(\text{org})}] - n \log[\text{H}^+] \quad (7)$$

Since $\text{pH} = -\log[\text{H}^+]$; equation (7) can be re-written as;

$$\text{Log } D = \text{Log } K_{\text{ex}} + n \log[\text{HBPpy}_{(\text{org})}] + np\text{H} \quad (8)$$

From equation (8), therefore; plots of log D versus log $[\text{HBPpy}_{(\text{org})}]$ or pH are linear, with slopes (n) equal to the number of moles of ligands involved in the complexation and the number of protons (H^+) displaced from the acidified aqueous solution of the metal ions studied.

Again, from equation (8);

$$\text{Log } K_{\text{ex}} = \text{Log } D - n \log[\text{HBPpy}_{(\text{org})}] - np\text{H} \quad (9);$$

from which the data in Table 1 were obtained.

3. 0. Results and Discussion

3.1. Dependence of solvent extraction on ligand concentrations

The data on the logarithms of the distribution ratios (D) and the extraction equilibria (K_{ex}) are presented on Table 1.

Table 1. Data on the logarithms of the distribution ratios (D) and extraction equilibria (K_{ex}) of the metal ions from their aqueous solutions at various concentrations of the HBPpy ligand at pH 4.

[HBPpy]	$\text{VO}_2(\text{BPy})_2$		$\text{La}(\text{BPy})_3$	
Log [HBPpy]	Log D	Log k_{ex}	Log D	Log k_{ex}
-2.00	-1.06	-5.06	-1.38	-7.38
-1.70	-0.41	-5.01	-0.10	-7.00
-1.52	-0.18	-5.14	-0.29	-7.73
-1.40	0.07	-5.13	0.10	-7.70
-1.30	0.21	-5.19	0.37	-7.73
-1.22	0.37	-5.19	0.95	-7.39
-1.15	0.50	-5.20	1.06	-7.49
-1.10	0.60	-5.20	1.38	-7.32
-1.05	0.72	-5.18	1.69	-7.16
-1.00	0.79	-5.21	1.85	-7.15
-0.82	1.06	-5.30	2.00	-7.54
-0.70	1.69	-4.91	2.70	-7.20

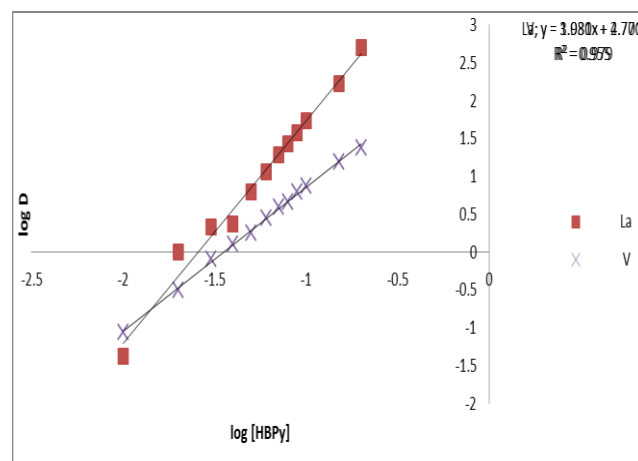


Figure 1. Plot of log of distribution ratios, D of the La and V ions versus log of HBPpy concentrations at pH 4.

The results presented in Figure (1) show that the distribution ratio, D is a function of number of moles (n) of the ligand concentrations as presented in equation (8). The values of n determined from the slopes of the plots of log D versus log $[\text{HBPpy}_{(\text{org})}]$ gave 3.08 for La (III) and 1.93 for V(V). Hence, approximately 3 moles of the HBPpy ligand reacted with one mole of La^{3+} while 2 moles of the same ligand reacted with VO_2^+ during the extraction process. This may have indicated that the metal ions existed as hydrated mononuclear species in the aqueous phase while the species extracted into the organic phase were $\text{La}(\text{BPy})_3$ and $\text{VO}_2(\text{BPy})_2$.

The average logarithms of the equilibrium constant (K_{ex}) values obtained for the metals at the different HBPpy concentrations and a buffer of 4 (Table 1) are -7.40 (La) and -5.14 (V); showing that the ligand is more efficient in the recovery of V(V) than the La(III) from the aqueous solution. This could be due to the greater attraction of the ligand by the V(V) as a result of its smaller ionic radius than the La(III) ion. Similar observation had been reported elsewhere⁹.

3.2. Dependence of Extraction on pH

The data on the logarithms of the distribution ratios (D) and the extraction equilibria (K_{ex}) on the extraction of the metal ions at different pH of their aqueous solutions using 0.02 M of the HBPpy are presented on Table 2, while the

graphs are shown on Figure 2.

Table 2. Data on the logarithms of the distribution ratios (D) and the extraction equilibria of the V(V) and La(III) ions at different pH of their aqueous solutions using 0.02 M of the HBPY ligand.

pH	VO ₂ (BPy) ₂		La(BPy) ₃	
	Log D	Log K _{ex}	Log D	Log K _{ex}
0.0	-1.38	2.02	-1.38	3.72
1.0	-1.19	0.21	-0.95	1.15
2.0	-0.87	-1.47	-0.60	-1.50
2.5	-0.60	-2.20	2.00	-0.40
3.0	0.95	-1.65	2.70	-1.20
3.5	2.40	-1.20	2.70	-3.00
4.0	3.00	-1.60	2.40	-4.90
4.5	3.00	-2.60	2.00	-6.40
5.0	2.70	-3.90		

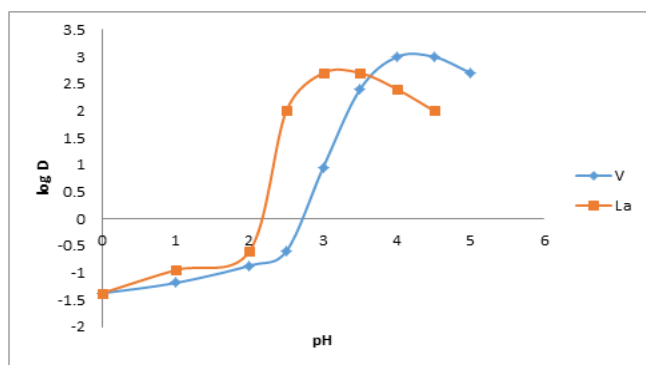


Figure 2. Plots of logarithms of distribution ratios, D of the metallic ions versus pH at 0.02 M of HBPY concentrations.

From the graphs on Figure 2, it could be observed that extractability of the metal ions increased with pH, reaching a maximum at the pH 3.0 and 4.0 for the La and V respectively, but decreased markedly at higher pH values. The rising portion of the log D versus pH curve reflects the presence of cationic species. Below the pH 3.0 and 4.0, the metal-aquo and the metal-ligand complex cations of the type $[M(H_2O)_x]^{n+}$ and $[ML_{n-1}]^+$, etc., become dominant species. Within the pH range of 3.0 – 3.5 for La and 4.0 - 4.5 for V, where log D is constant, the neutral chelates, $M(BPy)_n$ prevail at equilibrium. At higher pH values, however, hydrolysis of the metal ions would occur with the formation of one or more of a series of metal-hydroxo complexes (e.g. $[M(OH)]^{n-1}$, $[M(OH)_2]^{n-2}$, ... which are non-extractable, hydrophilic, anionic products. Similar reports have been made^{3, 10, 11}.

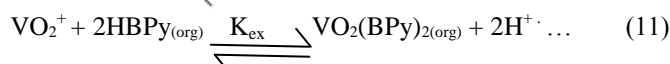
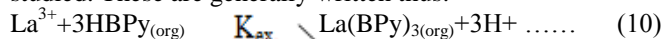
The rising portion of the log D versus pH curve (Figure 2) gave the slopes of 3.08 for La(BPy)₃; and 2.15 for the VO₂(BPy)₂. These values; (again, approximately 3.0 and 2.0 for the La and V respectively) indicated that three and two moles respectively of H⁺ ions were released per mole of La(III) and V(V) respectively on the formation of the extractable complexes by the ligand. Again, this confirms the formation of simple metal chelates; La(BPy)₃ and VO₂(BPy)₂. Similar metal chelates have been observed by many investigators in the extraction of metals with acylpyrazolones^{12, 13}.

The average values of log K_{ex} are La(BPy)₃ = -0.49; and VO₂(BPy)₂ = -1.39. This is indicative that at the pH range of investigation and at 0.02 M concentration of the ligands, La(III) was more quantitatively extracted by the butanoylpyrazolone than the V(V) ion. This could be attributed to the larger ionic charge and the atomic number/atomic mass of the La(III), This means that the V(V) ions with smaller ionic radius attract more OH⁻ of the H₂O

molecules of the aqueous solution, thus remaining hydrophilic. This shows that the pH of the aqueous solution of the metal ion affect the extraction of the metal ions, in addition to other factors such as ionic charge, ionic radius and the atomic mass of metal ion.

4.0. Conclusion

The distribution behaviour of La(III) and V(V) as a function of ligand concentration and pH of the aqueous phase were studied and the slopes of 3 and 2 obtained from the plots of log D versus log [HBPY] and pH indicated that La(III) interacted with the ligand in the 1:3 mole ratio while the V(V) or VO₂⁺ interacted at 1:2 metal-ligand mole ratio. The extraction process involves, therefore, three and two moles respectively of H⁺ ions per mole of La(III) and V(V) extracted. On substitution of the values of the slopes into equation (1), we get the appropriate valid balanced equations for the solvent extraction processes of the metallic ions studied. These are generally written thus:



It can be inferred from the study that the metal ions studied can quantitatively be separated from each other in their aqueous solutions or in the presence of other metallic ions by proper adjustment of the extractant concentrations and pH, thereby providing a clear method of purifying and concentrating materials containing these metal ions for electrowinning and extraction.

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