

The Solvent Extraction of Divalent Metals with 1-Phenyl-3-Methyl-4-Trifluoroacetylpyrazol-5-one and TOPO as the Group Separation and Concentration Methods of Trace Metals

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The synergistic extraction of divalent metal ions with 1-phenyl-3-methyl-4-trifluoroacetylpyrazol-5-one (HPMTEP) and TOPO in cyclohexane was examined in order to obtain the preliminary knowledge on the group-extraction and concentration methods of trace elements in natural waters. More than 98 percent of the divalent metal ions examined (Cu^{2+} , Mn^{2+} , Zn^{2+} , Co^{2+} , Pb^{2+} , Cd^{2+} , Fe^{2+} and Ni^{2+}) were extracted at the pH from 1.5 to 2.8 with 0.02 M HPMTEP and 0.01 M TOPO, and even alkaline earths (Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+}) were extracted quantitatively at the pH from 2.4 to 4.0 with 0.05 M HPMTEP and 0.01 M TOPO.

KEY WORDS: 1-Phenyl-3-methyl-4-trifluoroacetylpyrazol-5-one/ Solvent extraction/ Divalent metals/

INTRODUCTION

4-Acylpyrazol-5-ones, which are structurally similar to β -diketones such as acetylacetone and thenoyltrifluoroacetone (HTTA), have been proved promising reagents for extracting the chelates of metals from acidic media.^{1~21)} In particular, fluoro-substituted 4-acylpyrazolone is expected to be useful as an extracting reagent owing to the electron-attracting effect of fluorine atoms. Hasany and Qureshi¹⁵⁾ had examined the extractability of group IB, IIB and IIIA-VA elements with 1-phenyl-3-methyl-4-trifluoroacetylpyrazol-5-one (HPMTEP); this reagent was found to be poorer than HTTA in metal extractability.

It is evident from the previous papers^{18~20)} that the synergic extraction as TOPO adducts of acylpyrazolonates is very effective for the extraction of especially divalent metal ions. In the present paper, the main purpose is to examine the extraction of divalent metal ions using HPMTEP and TOPO as the methods for group-extracting and concentrating the trace elements from natural waters.

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EXPERIMENTAL

Reagents

HPMTFP was synthesized from 1-phenyl-3-methylpyrazol-5-one and trifluoroacetic anhydride according to the Jensen's method.¹⁾ The crude product was purified by recrystallizing twice from aqueous dioxane, and the analytical data was shown in the previous paper.¹⁸⁾ TOPO was purchased from Dojindo Co., Ltd., Research Laboratories. All other materials were reagent-grade and used without further purifications.

Procedures

The extractions were carried out between 10 ml of buffered solution containing appropriate amounts of metal ions and the same volume of cyclohexane solution containing 0.02 or 0.05 M HPMTFP and 0.01 M TOPO. The aqueous solution was made to have 0.01 M acetic acid-sodium acetate buffer and 0.1 M sodium perchlorate, and its pH was adjusted to a suitable value. The two phases were shaken by means of a mechanical shaker for 1 hr at 25°C. The aqueous concentrations of metal ions were determined using a Japan Jarrell-Ash Model AA-781 Atomic Absorption Spectrometer and Hitachi Polarized Zeeman Atomic Absorption Spectrometer Model 180-80, and the metal concentrations in the organic phase were similarly obtained by stripping with 1 M hydrochloric acid and using the same method as that for the aqueous phase. The pH of the aqueous phase was checked after extraction process.

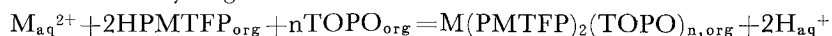
RESULTS AND DISCUSSION

Cyclohexane was used as the organic phase in the present work because the adduct formation of β -diketonates was most stable in cyclohexane,²²⁾ and the synergistic extraction of acylpyrazolonates was more enhanced in cyclohexane than in benzene.²⁰⁾

The solvent extraction of most divalent metals other than Cu^{2+} using only HPMTFP solution in cyclohexane was very low or not so high. However, the extraction of these metals was much enhanced when a mixture of HPMTFP and TOPO was used.

The extraction curves of VO_2^+ , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} with 0.02 M HPMTFP and 0.01 M TOPO in cyclohexane were shown in Figs. 1-3. Only VO_2^+ was not perfectly extracted, but the other divalent metals were extracted quantitatively at the pH value more than 3. As can be seen in Fig. 4, Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} were extracted completely by 0.05 M HPMTFP and 0.01 M TOPO in cyclohexane.

Figures 5-8 indicated the log D vs. pH plots in the synergistic extraction of the metals examined. The slopes of the linear plots for Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} were very close to 2, theoretical value. This indicates that two hydrogen ions are released in the formation of each chelate.



where subscripts aq and org denote the aqueous and organic phases, respectively.

In the extraction of Fe^{2+} , hydroxylammonium chloride was added to the aqueous

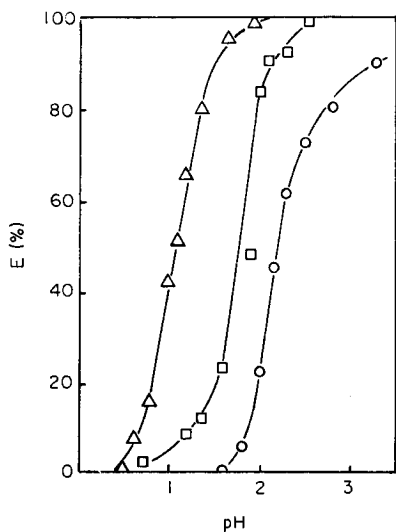


Fig. 1. Extraction of Mn(II), Fe(II) and V(V) chelates as a function of pH. Org. phase: HPMTFP 0.02 M, TOPO 0.01 M in cyclohexane, aq. phase: NaClO₄ 0.1 M, CH₃COONa 0.01 M, (○) VO₂⁺ (△) Mn²⁺, (□) Fe²⁺.

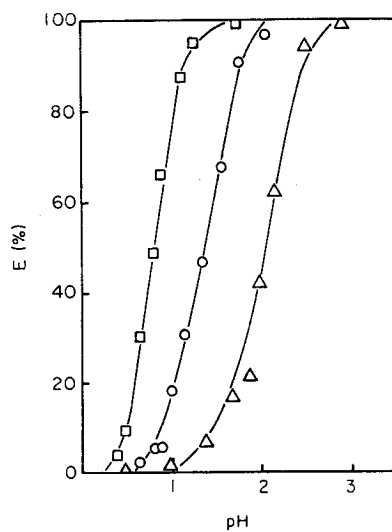


Fig. 2. Extraction of Cu(II), Co(II) and Ni(II) Conditions are the same as in Fig. 1. (○) Co²⁺, (△) Ni²⁺, (□) Cu²⁺.

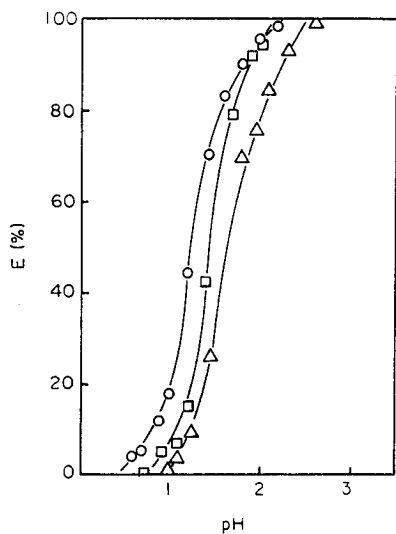


Fig. 3. Extraction of Zn(II), Pb(II) and Cd(II). Conditions are the same as in Fig. 1. (○) Zn²⁺, (△) Cu²⁺, (□) Pb²⁺.

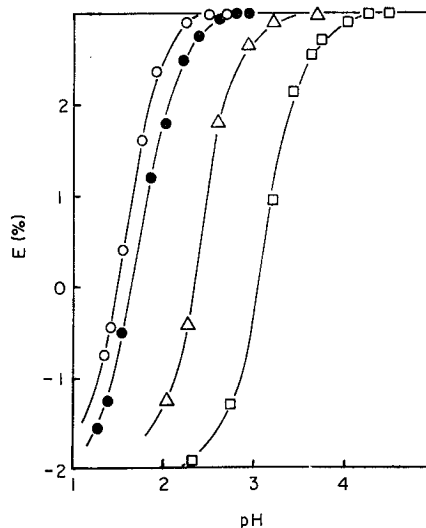


Fig. 4. Extraction of Mg(II), Ca(II), Sr(II) and Ba(II). Org. phase: HPMTFP 0.05 M, TOPO 0.01 M in cyclohexane, aq. phase: NaClO₄ 0.1 M, CH₃COONa 0.01 M, (○) Mg²⁺, (●) Ca²⁺, (△) Sr²⁺, (□) Ba²⁺.

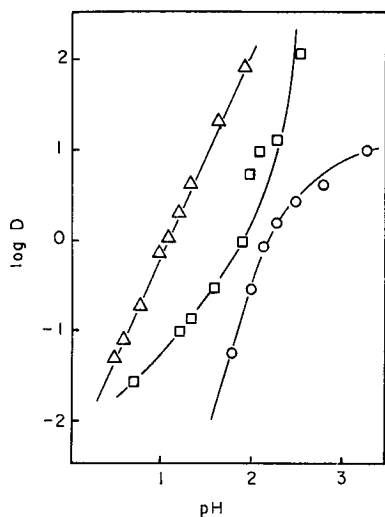


Fig. 5. Logarithm of the distribution ratio of Mn(II), Fe(II), and V(V) chelates as a function of pH. Conditions are the same as in Fig. 1.
(○) VO_2^+ , (Δ) Mn^{2+} , (\square) Fe^{2+} .

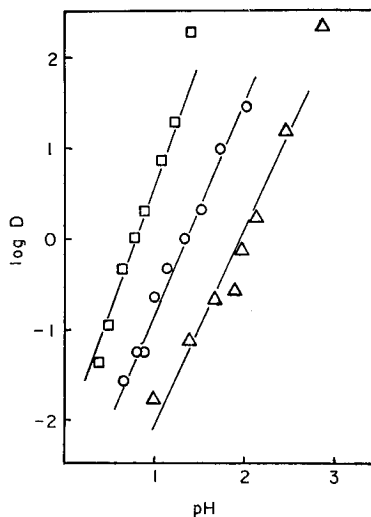


Fig. 6. Extraction of Cu(II), Co(II) and Ni(II). Conditions are the same as in Fig. 1.
(○) Co^{2+} , (Δ) Ni^{2+} , (\square) Cu^{2+} .

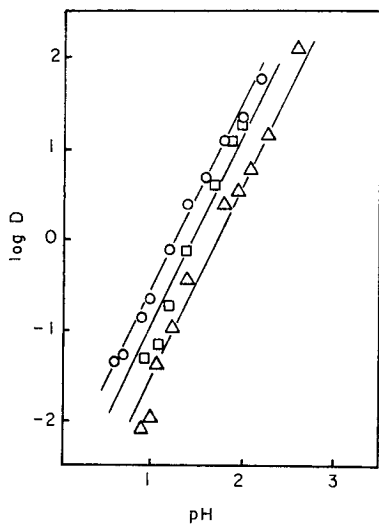


Fig. 7. Extraction of Zn(II), Pb(II) and Cd(II). Conditions are the same as in Fig. 1.
(○) Zn^{2+} , (Δ) Cd^{2+} , (\square) Pb^{2+} .

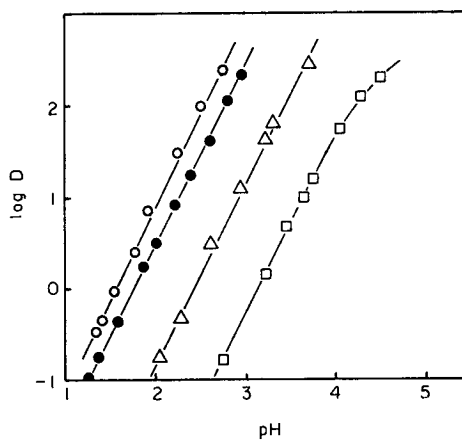


Fig. 8. Extraction of Mg(II), Ca(II), Sr(II) and Ba(II). Conditions are the same as in Fig. 4. (○) Mg^{2+} , (●) Ca^{2+} , (Δ) Sr^{2+} , (\square) Ba^{2+} .

phase in order to keep the ferrous ion divalent. However, as shown in Fig. 5, the deviation from the theoretical slope, 2, in the extraction curve of Fe^{2+} is probably caused by the incompleteness of the reduction reaction of the ferric ion. In the VO_2^+ extraction, the decrease in distribution ratio at higher pH may be due to the formation of the non-extractable anion such as VO_3^- .

Table I. Extraction of metals with 4-acylpyrazolones and β -diketones

Metal ion	0.02 M HPMTFP 0.01 M TOPO (cyclohexane)			0.2 M HTTA** (benzene)	0.1 M HDBM** (benzene)	1% HPMBP*** (chloroform)
	pH _{0.02}	pH _{0.50}	pH _{0.98}	pH _{0.50}	pH _{0.50}	pH _{0.50}
Mn ²⁺	0.3	1.1	1.9		7.80	4.3
Fe ²⁺	0.8	1.9	2.4			
Co ²⁺	0.6	1.4	2.2	4.1	6.40	4.3
Ni ²⁺	1.3	2.05	2.8	5	6.4	4.4
Cu ²⁺	0.3	0.75	1.5	1.38	2.90	1.2
Zn ²⁺	0.45	1.3	2.15		6.4	3.3
Cd ²⁺	1.0	1.75	2.55		8.0	4.5
Pb ²⁺	0.7	1.5	2.3	3.34	5.6	2.7
Mg ²⁺	0.68*	1.50*	2.36*		8.50	6.6
Ca ²⁺	0.94*	1.78*	2.64*	6.7	9.9	6.6
Sr ²⁺	1.58*	2.40*	3.26*	7.8	11.1	7.6
Ba ²⁺	2.32*	3.16*	4.02*	8	12	10
VO ₂ ⁺	1.6	2.15		3.3		1.3

* 0.05 M HPMTFP + 0.01 M TOPO, ** Taken from Ref. (3), *** Taken from Ref. (21).

Table I summarized the pH_{0.02}, pH_{0.50}, and pH_{0.98}, values (pH values at which 2, 50 and 98 percent of the metal ion were extracted, respectively) of the metal ions which were extracted with 0.02 or 0.05M HPMTFP and 0.01M TOPO in cyclohexane. The pH_{0.50} values in the case of dibenzoylmethane (HDBM), thenoyltrifluoroacetone (HTTA) and 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (HPMBP) were also compared in Table I.³⁾ As shown in the table, when a mixture of HPMTFP and TOPO was used, most divalent metal ions tested were extracted quantitatively around pH 3, and even barium ion which is noted as one of most poorly extractable metal ions could be extracted almost perfectly above pH 4.0.

The present synergistic extraction seems to be promising as the group-separation and concentration methods of trace elements in natural water for the emission spectrometry such as ICP-AES.

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