EXTRACTION OF SCANDIUM, YTTRIUM AND INDIUM WITH 1-PHENYL-3-METHYL-4-BENZOYLPYRAZOL-5-ONE

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Distribution of 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (HA) between aqueous phase (ionic strength 0·1 or 1·0) and organic phase (n-octane, tetrachloromethane, isoamyl alcohol or cyclohexane) has been investigated; the respective distribution constants of HA have been calculated. From the distribution of scandium, yttrium and indium between aqueous phase of ionic strength 0·1 and 1·0 (perchlorate medium) and benzene – n-octane – isoamyl alcohol and cyclohexane – tetrachloromethane, respectively, it has been found that complexes MA_n are formed in aqueous phase, and complexes MA_3 are transferred to the organic phase (M = Sc, Y and In). Extraction and distribution constants of the individual complexes have been determined along with their stability constants in aqueous phase. Influence of tri-butyl phosphate, tri-n-butylphosphine oxide, tri-n-octylphosphine oxide, pyridine, quinoline, isoquinoline, methyl isobutyl ketone, and isoamyl alcohol (S) on extraction of the above-mentioned complexes has been investigated, and several addition constants of complexes $MA_3.S$ and $MA_3.S_2$ have been determined.

Our previous report[1] dealt with extraction of chelate complexes of HA with some trivalent metal cations. This paper complements the previous studies by further complexes of HA with scandium, yttrium and indium also in the presence of synergists, and it deals with determination of distribution constants of HA.

Whereas complexes of yttrium have been given no attention so far, extraction of scandium from aqueous perchlorate and phthalate media in organic solvents was studied, and the respective values of extraction constants were calculated[2,3]. Furthermore, also influence of tetraethyldiamidoheptyl phosphate acting as the extraction synergist was studied[4]. Similarly extraction of indium from aqueous perchlorate medium was investigated[5].

EXPERIMENTAL

Reagents and Apparatus

Preparation and purification of HA were described elsewhere[6]. Its solutions as well as those of S in organic phase were prepared from accurate weighings. The other chemicals were of *p.a.* purity grade; isoquinoline and isoamyl alcohol were distilled. pH of the aqueous phase was adjusted by means of $HClO_4$, $NaClO_4$ and NaOH solutions to make the final ionic strength 0·1 or 1·0.

Stock solutions of ^{46}Sc(ClO$_4$)$_3$, ^{114}In(ClO$_4$)$_3$ and ^{90}Y(ClO$_4$)$_3$ were prepared from commercial samples of ScCl$_3$, InCl$_3$ and YCl$_3$, respectively, by evaporation of excess HCl and transferring to HClO$_4$. Their concentrations and activities of the measured solutions were for Sc: $8 . 10^{-7}$M and $(8$ to $10) . 10^3$ s^{-1} mol^{-1}; for In: $6 . 10^{-6}$M and $(3$ to $5) . 10^3$ s^{-1} ml^{-1}; for Y: $1 . 10^{-9}$M and $(2$ to $8) . 10^3$ s^{-1} ml^{-1}.

Gamma radiation of Sc and In was measured with a Tesla NAQ 232 probe connected with a counter VAM 15D Vakutronik (GDR), beta radiation of yttrium was measured with a Tricarb 2425 Packard instrument (U.S.A.). Spectrophotometry was carried out with a Spectromom 20 and quartz cells (MOM Budapest). pH of the aqueous phase was measured potentiometrically with an EIL apparatus and GHS 23 and RJ 23 electrodes (GB).

Procedure

Equal volumes of aqueous and organic phases (5 or 10 ml) were stirred 12 h at $21 \pm 1°$C; according to preliminary experiments this time was sufficient for the extraction equilibrium to be established. After separation of the phases an aliquote was taken from each and was measured (in the case of Sc and In) in glass ampoules in a NaI(Tl) well crystall. The yttrium radioactivity was measured as follows. The aliquote portion of aqueous phase (2 ml) was mixed with 2 ml HA solution in the given organic solvent and with 10 ml methanol. Both the initial HA concentration and organic solvent were the same as those in the measured sample from which the aliquot portion of aqueous phase was withdrawn. The mixture thus obtained was measured in a glass ampoule by means of the scintillation detector, and the result was compared with a calibration curve. In similar way 2 ml 0·1M-NaClO$_4$ and 10 ml methanol were added to the aliquot portion (2 ml) of the organic phase. pH was measured in the remaining volume of aqueous phase.

For determination of the distribution constants of HA equilibrium between the both phases was established, whereupon a defined part of the aqueous phase was withdrawn carefully, and the present HA was reextracted in pure organic solvent. Comparison of the measured absorbance (at 290, 275 and 242 nm for tetrachloromethane, isoamyl alcohol, and n-octane – cyclohexane, respectively) with the calibration curves gave the equilibrium HA concentrations. The distribution constants of the reagent, $K_D(HA)$, were then calculated from the relation $K_D(HA) = c_{HA} — [HA]'_{org}(1 + K_D(HA)^{-1})/[HA]'_{org}(1 + K_D(HA)^{-1})$, where c_{HA} means the initial HA concentration, and $[HA]'_{org}$ stands for its concentration in organic phase found after extraction of the equilibrium aqueous phase. The calculation can be simplified by neglecting the $K_D(HA)^{-1}$ value as compared with unity; this was made possible by the preliminary finding that the $K_D(HA)$ value in the investigated systems is greater than 100. The calculation procedure of the extraction, stability, and addition constants was the same as in ref.[1]

RESULTS AND DISCUSSION

Distribution of the Reagent between Organic and Aqueous Phases

The distribution constants $K_D(HA)$ of the reagent between aqueous phase of pH 2·3 and cyclohexane, n-octane, tetrachloromethane or isoamyl alcohol were determined. In this pH region both protonation and dissociation of the reagent are suppressed in favour of the form HA. The found values are given in Table I; the single comparable literature date of $K_D(HA)$ for isoamyl alcohol[2] agrees with our result in its order of magnitude.

For mutual comparison of the so far determined $K_D(HA)$ values the dependence formulated by Hildebrand and Scott[7] was chosen: $\log\left(K_D(HA)/(\delta_{aq} - \delta_{org})\right) = A\delta_{org} + B$; δ_{aq} and δ_{org} are solubility parameters of water and the organic solvent,

TABLE I

Values of Distribution Constants $K_D(HA)$
$t = 21°C$.

Organic phase	Ionic strength I	$\log K_D(HA)$
n-Octane	0·1	2·16
	1·0	2·02
Cyclohexane	0·1	2·14
Tetrachloromethane	0·1	2·52
Isoamyl alcohol	0·1	2·69
	1·0	2·33^a

^{a} From ref.[2] for $t = 25°C$.
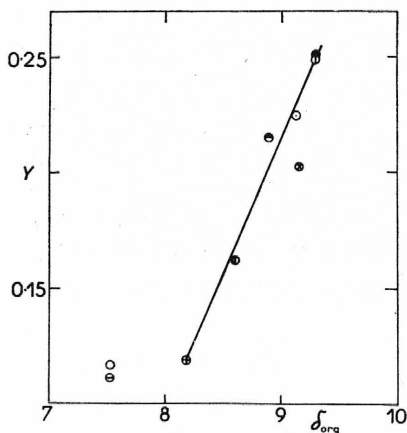
FIG. 1

Dependence of $Y = \log\left(K_D(HA)/(\delta_{aq} - \delta_{org})\right)$ on δ_{org}

Ionic strength 1·0: ⊗ benzene, ● chloroform, ⊖ n-octane, ionic strength 0·1: ⊙ benzene, ⊘ chloroform, ○ n-octane, ◓ toluene, ⊕ cyclohexane, ◐ tetrachloromethane.
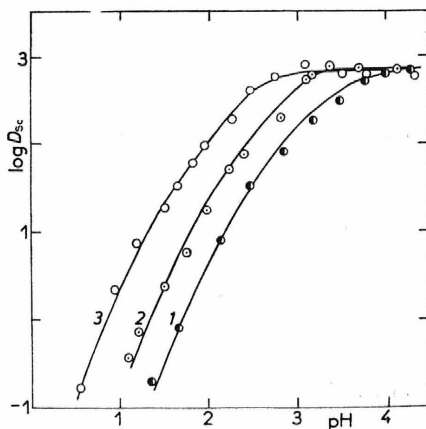

FIG. 2

Distribution of Scandium between Solutions of HA in Benzene and 1·0M-NaClO$_4$–HClO$_4$
c_{HA}: curve *1* $1 . 10^{-3}$M, *2* $3 . 10^{-3}$M, *3* $1 . 10^{-2}$M.

respectively, A and B are constants. This dependence is represented in Fig. 1. The $K_D(HA)$ values for $I = 0.1$ and individual organic solvents were taken from literature: benzene[8], toluene[1], chloroform[9]; for $I = 1.0$: benzene[2], isoamyl alcohol[2], chloroform[9]. Obviously the $K_D(HA)$ values found for $I = 0.1$ agree well with the above relation except for n-octane. No analogous conclusions can be drawn for $I = 1.0$ due to small number of the determined values.

Extraction of MA_n *Complexes*

Figs 2 to 4 give curves of dependences $\log D_M = f(pH)$ for various analytical concentrations of HA in benzene $(c_{HA}$ within $1 \cdot 10^{-3}$ to $1 \cdot 10^{-2}$M) at $I = 1.0$ (Sc, In) or 0.1 (Y). Therefrom it follows that in the mentioned c_{HA} interval and pH region successive formation of MA^{2+}, MA_2^+ and MA_3 complexes must be considered in aqueous phase as well as subsequent extraction of MA_3 in the organic phase. Similar relations were found for n-octane, toluene, tetrachloromethane and chloroform as solvents, using the ionic strength $I = 1.0$ and 0.1, too. Using the known pK_{HA} and $K_D(HA)$ values, the above extraction curves were transformed first into curves of the dependences $\log D_M = f(pA)$ where $pA = -\log [A^-]$, and therefrom the corresponding stability constants $\beta_n = [MA_n]/[M][A]^n$ were calculated by the

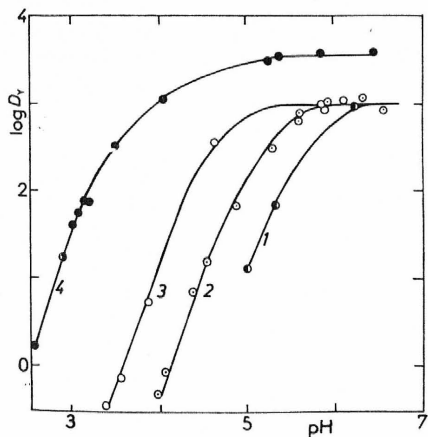FIG. 3

Distribution of Yttrium between Solutions of HA in Benzene and Isoamyl Alcohol and 0.1M-NaClO$_4$-HClO$_4$ or NaOH

c_{HA}: benzene: curve *1* $1 \cdot 10^{-3}$M, *2* $3 \cdot 10^{-3}$M, *3* $1 \cdot 10^{-2}$M; isoamyl alcohol: curve *4* $3 \cdot 10^{-3}$M.
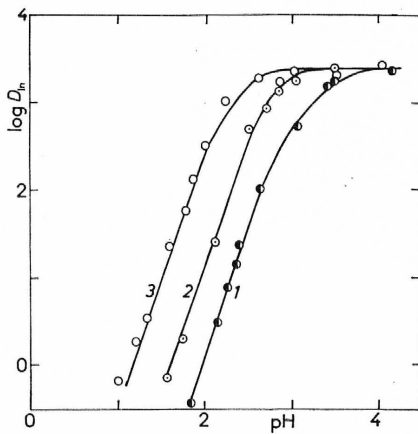
FIG. 4

Distribution of Indium between Solutions of HA in Benzene and 1.0M-NaClO$_4$--HClO$_4$

c_{HA}: curve *1* $1 \cdot 10^{-3}$M, *2* $3 \cdot 10^{-3}$M, *3* $1 \cdot 10^{-2}$M.

method of two parameters[10] (in the latter equation charges are omitted for simplicity). The obtained values are given in Table II along with $K_D(MA_n)$ and K_{ex} values. Use of n-octane as the organic solvent neccessitated to work with saturated HA solutions; here the reproducibility of individual experimental points was somewhat decreased.

With isoamyl alcohol as solvent an anomalous course of extraction curves of yttrium is found, they are shifted to lower pH values (Fig. 3, curve 4). We presume it to be due to synergic extraction of the complex type $YA_3.S_n$ where S means isoamyl alcohol, which is discussed later in the text.

Our results (Table II) can be compared with those of other authors to a limited extent. The β_3 value of the indium complex is practically identical with results of Zolotov and Gavrilova[5]. It is interesting to compare values of the extraction constants of the studied elements with the use of HA and 2-thenoyltrifluoroacetone (HTTA).

TABLE II

Stability Constants, Extraction and Distribution Constants of Complexes MA_n

Ionic strength I	Solvent	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log .K_D(MA_n)$	$\log K_{ex}$	$\log K_{ex}$ for HTTA[a]
			Scandium				
0·1	benzene	7·4	14·5	21·2	2·7	2·0	—0·8
	isoamyl acohol	7·4	14·3	20·8	2·5	3·0	—
	n-octane	7·0	13·3	19·1	2·4	2·5	—
1·0	benzene	7·4	14·4	21·0	2·8	3·8	—
	isoamyl alcohol	7·5	14·4	20·7	3·0	4·6	—
	n-octane	6·8	13·3	19·5	2·7	4·0	—
			Yttrium				
0·1	benzene	5·7	10·7	14·9	3·0	—4·8	—6·8
	chloroform	5·8	10·6	14·5	3·6	—5·3	—
	toluene	5·5	10·4	14·6	2·9	—5·1	—
	cyclohexane	—	—	—	3·3	—2·7	—
	tetrachloromethane	—	—	—	3·2	—4·0	—
			Indium				
1·0	benzene	6·9	14·0	20·6	3·4	2·8	—4·3

[a] From ref.[11], HTTA — thenoyltrifluoroacetone.

From Table II it follows that K_{ex} values are higher when HA is used, *i.e.* under comparable conditions the extraction takes place from more acidic medium of the aqueous phase.

Extraction of $MA_n.S_s$ *Complexes*

Theoretical aspects of extraction of the complexes $MA_n.S_s$ are dealt with in ref.[1]. The complexes type MA_n show coordination unsaturation, free positions of the coordination sphere being occupied by molecules of water or organic solvent. These molecules are replaced, if another suitable neutral complex-forming reagent is used, which can result in increasing of distribution ratio of the central atom. The corresponding constant describing this process is given by the relation $\varkappa_s = [MA_n.S_s]_{org}$: : $[MA_n]_{org} [S]_{org}^s$. In this work we dealt with synergic extraction of scandium, yttrium and indium using the following neutral reagents: tri-n-butyl phosphate (TBP),

TABLE III

Formation Constants of the Adducts $MA_n.S_s$ in Benzene

Ionic strength I	pH	The added compound	$\log \varkappa_1$	$\log \varkappa_2$
		Scandium		
1·0	1·06	quin	—	3·5
	0·87	TBPO	—	8·5
	1·11	TOPO	5·2	9·2
		Yttrium		
0·1	3·91	MIBK	1·4	—
	4·24	iAmOH	1·8	—
	4·00	isoquin	3·3	—
	4·00	py	5·8	—
	3·91	TBP	4·3	—
	4·00	TBPO	6·6	—
	4·00	TOPO	6·2	—
	3·72	TOPO	6·3	—
		Indium		
1·0	1·06	quin	—	4·0
	1·06	TBPO	—	7·5
	1·06	TOPO	4·2	7·4

tri-n-butylphosphine oxide (TBPO), tri-n-octylphosphine oxide (TOPO), pyridine (py), quinoline (quin), isoquinoline (isoquin), methyl isobutyl ketone (MIBK) and isoamyl alcohol (iAmOH). As solubility of these compounds (except for pyridine) is negligible in aqueous phase as compared with that in organic phase (benzene), it is possible, in our case, to consider their equilibrium concentration in organic phase as their analytical concentration. For pyridine the equilibrium concentration was determined experimentally as in our previous paper[12]. Table III gives the values $\varkappa_s$ of formation constants of the adducts which were determined graphically from the courses of the dependence $\log D_M = f(c_s)$. From Table III it follows that stability of the adducts increases approximately in the series MIBK < iAmOH < isoquin < < TBP < py < TBPO < TOPO. This order corresponds to that of increasing basicity of the mentioned compounds, as it is given in refs[13,14]. Position of organophosphorus compounds in the evaluation of formation constants of the adducts corresponds roughly to their properties. The higher basicity of trialkylphosphine oxides as compared with trialkyl phosphates can be made use of in extraction separation of elements. A certain anomaly is encountered in the case of higher stability of the adducts with TBPO as compared with the TOPO complexes of yttrium. Value of the formation constant of the adduct with isoamyl alcohol is noteworthy, too. Although it has obviously one of the smallest values out of the compounds used, a possibility of direct use of isoamyl alcohol as solvent must be anticipated.

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