

## EXTRACTION OF SOME METALS INTO SOLUTIONS OF 1-PHENYL-3-METHYL-4-BENZOYLPYRAZOLONE-5 IN FREON 113

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The partition of 1-phenyl-3-methyl-4-benzoylpyrazolone-5 (HA) between aqueous solutions of  $\text{HClO}_4$  and  $\text{NaClO}_4$ , ionic strength 0.1, and Freon 113 or its 2 : 1 mixture with benzene was studied. The logarithms of the HA distribution constants are  $2.84 \pm 0.10$  and  $3.39 \pm 0.15$  for the two organic phases, respectively. The extraction curves of cerium(III) and europium(III) revealed that in dependence on the pH of the aqueous phase, the metals are transferred into the organic phase in the form of the  $\text{MA}_3$  complexes ( $M = \text{Ce}, \text{Eu}$ ). The stability constants of the complexes  $\text{MA}_n$  in the aqueous phase were determined along with their distribution and extraction constants. For cobalt, zinc, and hafnium, a part of the extraction curves could only be studied, only the extraction constants were therefore determined. The sparing solubility of HA in Freon 113 can be circumvented by using a Freon-benzene mixture 2 : 1, which is still practically incombustible.

1-Phenyl-3-methyl-4-benzoylpyrazolone-5 (HA) has been applied since 1959 as a very good extracting agent for the separation of a number of metals<sup>1-3</sup>. It is part of the liquid organic phase, the solvent being usually a 1st class flammable material. With a view to lowering or complete elimination of the organic phase flammability hazard, we concentrated on the application of Freon 113 ( $\text{CCl}_2\text{F.CClF}_2$ ) as the solvent, and furthermore examined the extraction of HA with Co, Zn, Ce, Eu, and Hf, respectively.

### EXPERIMENTAL

#### Chemicals and Apparatus

The preparation and purification of 1-phenyl-3-methyl-4-benzoylpyrazolone-5 has been described<sup>4</sup>. As the organic phase served solutions of HA in Freon-benzene mixture 2 : 1 (initial reagent concentration in this mixture was  $3 \cdot 10^{-2} \text{ mol l}^{-1}$  in all cases) and solutions of HA in pure Freon (initial HA concentrations  $1 \cdot 10^{-2}$  to  $5 \cdot 10^{-4} \text{ mol l}^{-1}$ ). Freon 113 (Du Pont) was redistilled prior to use. Benzene (Lachema) was reagent grade purity. The pH of the aqueous phase was adjusted with  $\text{HClO}_4$ ,  $\text{NaClO}_4$ , and  $\text{NaOH}$  solutions, maintaining constant ionic strength of 0.1 (except for Hf).

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The radioactive indicators used were converted to perchlorates; their initial concentrations ( $\text{mol l}^{-1}$ ) and activities ( $\text{s}^{-1}$ ) were as follows:  $^{152+154}\text{Eu}$   $6.1 \cdot 10^{-10}$ ,  $2.53 \cdot 10^3$ ;  $^{144}\text{Ce}$   $3.1 \cdot 10^{-11}$ ,  $2.99 \cdot 10^3$ ;  $^{175+181}\text{Hf}$   $7.0 \cdot 10^{-10}$ ,  $5.80 \cdot 10^3$ ;  $^{60}\text{Co}$   $9.2 \cdot 10^{-10}$ ,  $1.16 \cdot 10^4$ ;  $^{65}\text{Zn}$   $2.9 \cdot 10^{-11}$ ,  $2.81 \cdot 10^3$ .

The gamma activity of the samples was measured with a scintillation detector using a well-type NaI(Tl) crystal  $45 \times 50$  mm. The counting rate was recorded by means of a laboratory measurement kit Tesla NZQ 714 T.

The pH values of the samples after the extraction were measured by using a pH-meter Radelkis (Hungary) equipped with glass and calomel electrodes. The calibration was made using commercial buffers. The photometric measurements of the equilibrium concentrations of HA were carried out on an instrument Spektromom 201 (MOM, Hungary) at the wavelength 385 nm.

### Working Procedure

Equal volumes of the aqueous and organic phases (10 ml) were agitated on a rotary shaking machine in glass test tubes fitted with polyethylene stoppers in a thermostat at the temperature  $20 \pm 1^\circ\text{C}$ . The shaking duration was established empirically based on tentative experiments; it was 8 h for Eu, Co, and Zn, 4 h for Hf, and 24 h for Ce. After the extraction and phase separation (after the establishing of the radioactive equilibrium in the case of Ce), 2 ml of each phase were placed in glass ampoules and their activity was measured. The relative standard deviation of all measurements did not exceed 2%. The pH was measured in the remaining aqueous phase.

The reagent distribution ratios  $K_D(\text{HA}) = [\text{HA}]_{\text{org}}/[\text{HA}]$  were determined by extraction, similarly as in the works<sup>5,6</sup>; the square brackets denote equilibrium concentrations, the subscript org refers to the components in the organic phase, without subscript are those in the aqueous phase.

## RESULTS AND DISCUSSION

### Determination of the HA Distribution Constant

For both systems — aqueous phase, ionic strength 0.1, and either pure Freon or Freon–benzene mixture 2 : 1 — extractions were accomplished at five different pH values within the region of pH 4.5–7.0. The equilibrium HA concentration in the organic phase was determined photometrically by comparing the observed absorbances with the calibration curves. In the region of lower pH values of the aqueous phase, where  $D_{\text{HA}}$  was greater than 100, the equilibrium concentration of HA in the aqueous phase was determined indirectly, by reextraction from a preselected volume of the aqueous phase into the pure solvent and determining the absorbance of the latter. The logarithms of the reagent distribution ratio  $D_{\text{HA}}$  were plotted against the pH, and taking  $\text{p}K_{\text{HA}} = 4.08$  (ref.<sup>5</sup>) the distribution constants of the reagent,  $K_D(\text{HA})$ , were determined from the plot to be  $2.84 \pm 0.10$  for Freon as the solvent and  $3.39 \pm 0.15$  for the Freon–benzene 2 : 1 mixture. It is apparent from these values that the reagent is better soluble in benzene than in Freon. The sparing solubility of the reagent in Freon can be circumvented by using a Freon–benzene mixture, and the ratio 2 : 1 still ensures practically incombustibility of the mixture.

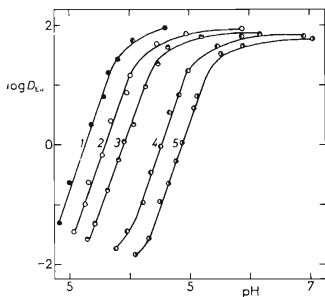


FIG. 1

Partition of Europium Between HA Solutions in Freon or Freon-Benzene Mixture 2:1 and 0.1M- $\text{NaClO}_4$ - $\text{HClO}_4$  or  $\text{NaOH}$   $c_{\text{HA}}$  ( $\text{mol l}^{-1}$ ): Freon:  $5.5 \cdot 10^{-4}$ ,  $4.1 \cdot 10^{-3}$ ,  $3.5 \cdot 10^{-3}$ ,  $2.1 \cdot 10^{-2}$ ; Freon-benzene:  $1.3 \cdot 10^{-2}$ .

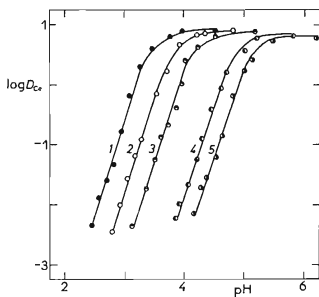


FIG. 2

Partition of Cerium(III) Between HA Solutions in Freon or Freon-Benzene Mixture 2:1 and 0.1M- $\text{NaClO}_4$ - $\text{HClO}_4$  or  $\text{NaOH}$   $c_{\text{HA}}$  and solvent used as in Fig. 1.

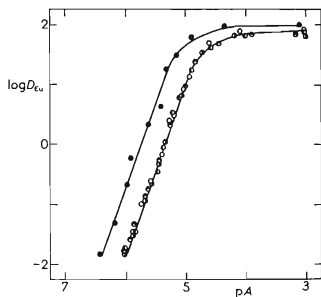


FIG. 3

Dependence of  $\log D$  on  $pA$  for Europium  $c_{\text{HA}}$  and solvent used as in Fig. 1.

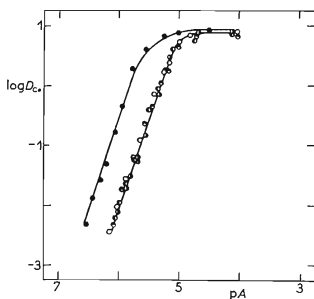


FIG. 4

Dependence of  $\log D$  on  $pA$  for Cerium  $c_{\text{HA}}$  and solvent used as in Fig. 1.

## Partition of Europium(III) and Cerium(III)

The extraction curves of the europium distribution ratio *versus* the pH for various initial concentrations of HA in the organic phase (Fig. 1) afforded approximately the same distribution ratios corresponding to the upper parts of the curves. The slopes of the ascending parts of the curves equal three. The dependences pertaining to cerium were alike (Fig. 2). On conversion of the pH values to  $pA$  ( $pA = -\log [A^-]$ ),

TABLE I

Stability, Extraction, and Distribution Constants of the  $MA_n$  Complexes

Ionic strength 0.1, temperature 20°C; organic phase A Freon, B Freon-benzene mixture 2 : 1, C benzene (or toluene, if indicated)<sup>1,2</sup>.

| Metal   | $\log K_D(MA_n)$ |     |                   | $\log K_{ex}$      |                    |                             | $\log \beta_1$ | $\log \beta_2$ | $\log \beta_3$ |
|---------|------------------|-----|-------------------|--------------------|--------------------|-----------------------------|----------------|----------------|----------------|
|         | A                | B   | C                 | A                  | B                  | C                           |                |                |                |
| Eu(III) | 1.9              | 2.0 | 3.15 <sup>a</sup> | -4.84              | -5.21              | -3.96<br>-4.87 <sup>a</sup> | 4.7            | 9.4            | 14.1           |
| Ce(III) | 0.9              | 0.9 | 2.80 <sup>a</sup> | -4.85              | -4.98              | -2.28 <sup>a</sup>          | 4.8            | 9.8            | 15.0           |
| Co(II)  | —                | —   | 1.42              | -9.35              | -8.67              | -7.38                       | —              | —              | —              |
| Zn(II)  | —                | —   | 3.57              | -8.83              | -8.31              | -5.35                       | —              | —              | —              |
| Hf(IV)  | —                | —   | —                 | 13.06 <sup>b</sup> | 10.11 <sup>b</sup> | 13.1 <sup>b</sup>           | —              | —              | —              |

<sup>a</sup> Toluene; <sup>b</sup> ionic strength 2.0.

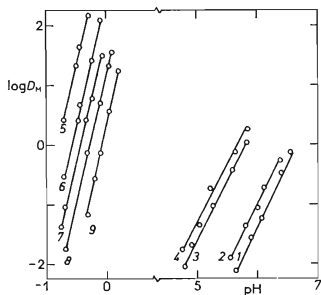


FIG. 5  
Partition of Cobalt(II), Zinc(II), and Hafnium(IV) Between HA Solution in Freon or Freon-Benzene Mixture 2 : 1 and 0.1M  $NaClO_4-HClO_4$  or NaOH (except for Hf, see text)

$c_{HA}$  ( $mol\ l^{-1}$ ): Freon: 1, 2,  $6.1 \cdot 10^{-2}$ ,  $7.5 \cdot 10^{-3}$ ,  $8.1 \cdot 10^{-3}$ ,  $9.5 \cdot 10^{-4}$ ; Freon-benzene: 3, 4,  $5.3 \cdot 10^{-2}$ ; 1, 3 cobalt, 2, 4 zinc, 5 to 9 hafnium.

where  $[A^-]$  is the equilibrium concentration of the species  $A^-$  in the aqueous phase – see, e.g., ref.<sup>5</sup>) and plotting the dependence of  $\log D_{Eu,Ce}$  versus  $pA$  (Figs 3, 4) it can be stated that the complexes  $MA^{2+}$ ,  $MA_2^+$ ,  $MA_3$  ( $M = Eu, Ce$ ) are formed consecutively in the aqueous phase, the last one being extracted into the organic phase. Furthermore, the corresponding stability constants  $\beta_n$  of the  $MA_n$  complexes in the aqueous phase were calculated from Figs 3 and 4 by means of the Dyrssen–Sillén method<sup>7</sup> and the distribution constants  $K_D(MA_3)$  of the  $MA_3$  complexes were determined as given in Table I. The extraction constants  $K_{ex} = (MA_3)_{org}[H^+]^3/[M^{3+}][HA]_{org}^3$  correspond then to the extraction of the above complexes, expressed by the scheme  $M^3 + 3(HA)_{org} \rightleftharpoons (MA_3)_{org} + 3H^+$ . Their values were calculated from the left, ascending part of the extraction curves, and are also given in Table I. A comparison of our results with the published data<sup>2,3</sup> pertaining to the extraction of the aforesaid metals into benzene or toluene shows that the extraction constants with Freon as the organic phase are at least one order of magnitude lower in all cases except hafnium. The stability constants of the complexes  $EuA_n$  in the aqueous phase are virtually identical with those reported in ref.<sup>8</sup>, for the  $CeA_n$  complexes our data differ from those reported by Efimov and coworkers<sup>9</sup> by at most two orders of magnitude, which can be looked upon as a satisfactory agreement, in view of the calculation method applied<sup>7</sup>.

#### *Partition of Cobalt(II), Zinc(II), and Hafnium(IV)*

The curves of the dependence of the zinc and cobalt distribution ratios logarithms on the pH of the aqueous phase were only studied in their ascending parts, because at higher pH values the radioactive indicators sorbed on the interface and the results were ill-reproducible. As in the preceding case, Freon or Freon-benzene mixture 2 : 1 was employed as the organic phase. The slope value of two indicates the occurrence of the metals as the  $Co^{2+}$  and  $Zn^{2+}$  species (Fig. 5, curves 1–4, as anticipated. For hafnium, the dependence of its distribution ratio on the initial concentration of the mineral acid was examined without adhering to the requirement of constant ionic strength (Fig. 5, curves 5–9). The  $K_D(HfA_4)$  value was not determined experimentally, since with the acidities of the aqueous phase that would have to be chosen the hafnium hydrolysis occurs to an extent.

The extraction constants were calculated from the extraction curves obtained for the three metals; they are given in Table I. For cobalt and zinc, the values are again lower than those pertaining to benzene as the organic phase.

It can be thus concluded that Freon 113 can serve well as an organic solvent for the extraction of metals with HA. The lower solubility of the reagent as well as of the extractable chelates can be eliminated by using a mixture Freon–benzene, ratio 2 : 1, which satisfies safety regulations as to the incombustibility of the organic phase,

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