EXTRACTION OF HAFNIUM BY 1-PHENYL-3-METHYL-4-BENZOYL-5-PYRAZOLONE FROM AQUEOUS-ALCOHOLIC SOLUTIONS*

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The hafnium extraction into solutions of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HL) in benzene, toluene, chloroform and tetrachloromethane from aqueous–alcoholic solutions of the formal acidity of 2M-$HClO_4$ was studied. Methyl, ethyl, n- and isopropyl, tert-butyl and allyl alcohol as well as ethylene glycol monomethyl ether and propylene glycol were used as the organic components of the mixed aqueous–organic phase. Their presence in some cases causes a synergic increase of the distribution ratio of hafnium. The explanation of this increase is presented on the basis of the results of the slope analysis, and measurements of the distribution of alcohols and of the relative permittivity of the organic phase. It suggests that the HfL_4 molecules are solvated by alcohol molecules in the organic phase. At high alcohol concentration the synergism changes into antagonism. This is caused by changes in the distribution of HL and its interaction with the alcohol in the organic phase.

Most of extraction studies published so far use two immiscible phases, both liquid at normal temperature, in which the main component of the organic phase is an organic solvent (diluent). The demands of nuclear technology stimulated research into high-temperature extractions where molten metals, salts or organic compounds are used as extraction phases. Recently, distribution between two non-aqueous phases, liquid at normal temperature, was studied. Even though these studies are theoretically interesting, the experimental difficulties as compared with common extractions from aqueous solutions makes them less attractive, so that systems such as liquid HF–hydrocarbons[1], liquid ammonia–tri-n-butyl phosphate[2], liquid ammonia–diethyl ether[3], high-molecular ammines in cyclohexane–dry methanol[4], di-iso-pentyl ether–acetonitrile[5] and nitromethane–decanol[6] are almost all which have been used in extractions of this kind.

Recently the application of an aqueous phase containing a miscible organic component has been introduced into extraction chemistry. Such media have been for some time in general use in ion-exchange studies and separations[7], nevertheless their application in extractions has been infrequent. Alian and Sanad[8] found that in the extraction of Ag(I), Hg(II), Zn(II), Co(II), Fe(III) and Se(IV) by tri(dodecyl)-amine and tri-n-butylphosphate in xylene, the addition of methyl and ethyl alcohol to the aqueous phase caused a decrease of the distribution ratio of these metals. The behaviour of Co(II) and Se(IV) is exceptional because their extractibility from 6M-HCl is

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increased by approximately one order of magnitude. Pronounced synergic effects have been found[9] in the extraction of Pa(V) by the same agents in the presence of methyl, ethyl and isopropyl alcohol, while the extraction of Pa(IV) by the solution of 2-theonyltrifluoroacetone in xylene was affected much less. The addition of acetone, on the other hand, caused a drop in the extractibility of Tb^{3+} by di(2-ethylhexyl)-phosphoric acid[10]. Lower aliphatic alcohols also increase the extractibility of the sulphate complexes of zirconium and hafnium into tri-n-butylphosphate[1]. Another data, however, point also to the possible effect of an organic component in the mixed phase on the extraction mechanism. Thus Bi(III) is extracted from acidic, bromide containing medium by di(2-ethylhexyl)phosphoric acid as solvated $BiBr_3$. On addition of ethanol or dimethylformamide, the extraction of solvated $HBiBr_4$ is preferred[12]. Despite so far unexplained effects of the organic component in such systems, their studies nevertheless are perspective even from the practical point of view. It has been shown[13] that the application of alcohol improves the separation of uranium, thorium and protactinium in the extraction by tri-n-octylamine.

As a part of systematic research of the extraction of hafnium, we have studied its extraction from aqueous–organic solutions by various chelate forming agents. In this paper, results of the extraction by 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HL) in benzene, toluene, chloroform and tetrachloromethane from aqueous–alcoholic solutions of the formal acidity of 2M-$HClO_4$ are reviewed and presented. As the organic component of the mixed aqueous–organic phase the following compounds were used: methyl, ethyl, n-propyl, isopropyl, tert-butyl and allyl alcohol as well as ethylene glycol monomethyl ether and propylene glycol.

EXPERIMENTAL

Reagents

As the extraction agent for hafnium HL, either commercially available (Lachema, Brno) or prepared by the method of Jensen[14] was used. The solvents used (benzene, toluene, $CHCl_3$, CCl_4), methanol, ethanol, propanol, and propylene glycol (of analytical reagent grade), isopropyl, tert-butyl, allyl alcohol and ethylene glycol monomethyl ether (of reagent grade) were all used without any further purification. Hafnium dioxide (99·8%) (K & K Laboratories, New York) was used for extraction experiments with macroconcentrations of hafnium.

Radioisotopes

As the radioactive indicator of hafnium, a mixture of nuclides $^{175+181}Hf$ in the form of oxide (USSR) was used. A stock solution of $^{175+181}Hf$ was prepared in 10M-$HClO_4$ (ref.[15]) with the hafnium concentration $\approx 10^{-4}$M and initial specific activity ≈300 μCi/ml. Actual working solutions were prepared by further dilution.

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* The term "polar phase" suggested by Alian[9] is later used in the text throughout to describe the aqueous–alcoholic phase. The term "organic phase" (low polar) has the usual meaning.

The distribution of alcohols was studied by using labeled compounds $^{14}CH_3OH$, n-C_3H_7OH-1-^{14}C (Kernforschungszentrum, Rosendorf, GDR) and C_2H_5OH-1-^{14}C (Amersham, England). The glass ampoules containing these substances were opened under cooling by liquid nitrogen or a mixture of solid carbon dioxide with acetone. Stock solutions were then prepared by rinsing out the ampoules with non-active alcohol into a volumetric flask. Specific activities of such solutions were approximately 8·4 μCi/ml for $^{14}CH_3OH$ and 1·0 μCi/ml for other two alcohols.

Apparatus

Gamma activity was measured using the VA-M-15D instrument with the electronic time preselector VAG-250 (both Vakutronik, Dresden, GDR) and a NAG 232 scintillation probe with a well-type crystal NaI(Tl) (Tesla, Czechoslovakia). β-Activity of alcohol samples labelled with ^{14}C was determined by a three-channel spectrometer TRICARB 3375 with external standardization (Packard, U.S.A.). The relative permittivity was measured using the dielectrometer OH 302 (Radelkis, Hungary) and ultraviolet spectra using the spectrophotometer Spectromom 201 MOM (Hungary).

Procedure

Hafnium extractions were carried out by the procedure described in previous papers[15,16]. Prior to extraction, the polar phase contained 0—70 v/v % alcohol, the radioactive indicator $^{175+181}Hf$ of ≈ 1·5 μCi activity and hafnium total concentration $1 \,.\, 10^{-6}$—$1 \,.\, 10^{-5}$M at the formal acidity of 2M-$HClO_4$. The organic phase was formed by a solution of HL in an organic solvent. The initial volume of each phase was 5 ml, time of agitation 48 hours. All extractions were carried out at 20°C.

The distribution ratio of hafnium (D), expressed as the ratio of γ-activities determined in 2 ml aliquots of organic and polar phases, was corrected for the volume changes which take place during the agitation by multiplying it by the ratio of equilibrium volumes of organic to polar phases. The volume changes were determined by agitation of non-active systems of identical composition in 10 ml graduated test tubes with 0·1 ml division with accuracy of approximately 2%. The relative standard deviation of γ-activity determinations was $\leq 2\%$.

The distribution of methyl, ethyl and n-propyl alcohol between polar and organic phases was measured using ^{14}C labeled alcohols. The composition of both phases was the same as in the hafnium extraction with the exception that instead of the $^{175+181}Hf$ indicator they contained the used alcohol labeled by 1·63 μCi $^{14}CH_3OH$, 0·49 μCi C_2H_5OH-1-^{14}C and 0·79 μCi n-C_3H_7OH-1-^{14}C, respectively. After 24 hours agitation aliquot amounts of the equilibrium organic phase was taken (2 ml for benzene and toluene but only 0·5 ml for $CHCl_3$ and 0·04 ml for CCl_4 since higher amount of the latter solvents quenched the scintillation of the measured samples) into a small flask made of low potassium glass, and 10—12 ml of a liquid scintillator (1·25 g of 2,5-diphenyloxazole and 0·05 g of 1,4-bis-(2,5-diphenyl-oxazolyl)benzene in 1 litre of toluene) were added. The relative beta activity was determined with a standard deviation of $\leq 2.5\%$. Using a known yield, found from the measurement of a series of quenched standards, the relative activity was converted to the absolute activity. From this and the absolute activity of the labeled alcohol used in each particular experiment the equilibrium alcohol concentration in the organic phase was calculated.

0·06M solution of hafnium perchlorate was prepared by melting HfO_2 with $K_2S_2O_7$, dissolving the solidified melt and by repeated precipitation of hafnium hydroxide by ammonia and by precipitate washing until the filtrate did not contain sulphates. After the final precipitation the precipitate was dissolved in perchloric acid and the concentration of hafnium determined gravimetrically as HfO_2.

RESULTS

Dependence of D on the Concentration of Alcohol

Fig. 1 shows the effect of the initial alcohol concentration (mol . l^{-1}) in the polar phase on the distribution ratio of hafnium in the extraction by the solution of HL in toluene. Analogous curves for extractions into benzene and CCl_4 are identical[17], and also those for the extraction into chloroform (Fig. 2) do not differ substantially from those of the former solvents. It is typical of most alcohols that they cause the synergic increase of *D*. The exceptions are n-C_3H_7OH and tert-C_4H_9OH for which the increase of extractibility is either negligible (tert-C_4H_9OH/benzene, tert-C_4H_9OH, n-$C_3H_7OH/CHCl_3$) or the value of *D* is constant over a wide alcohol concentration range (n-C_3H_7OH/benzene, n-C_3H_7OH, tert-C_4H_9OH/toluene and $CHCl_3$). The height of the synergic maximum increases in the series n-C_3H_7OH = tert-C_4H_9OH < iso-C_3H_7OH < C_2H_5OH < CH_3OH and the transition from one alcohol to another is the most pronounced in chloroform. Fig. 3 shows results of similar extractions in the presence of allyl alcohol and glycols.

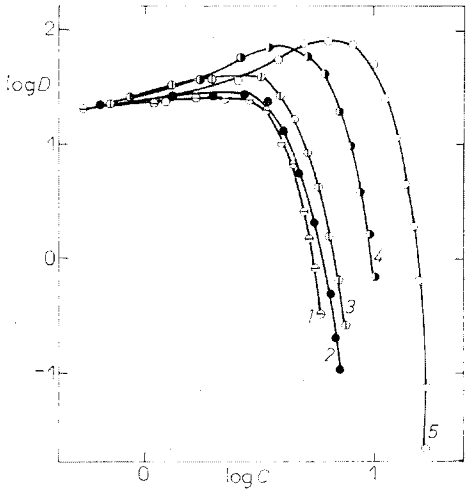


FIG. 1

Dependence of Hafnium Distribution Ratio (*D*) on the Initial Concentration of Alcohol (*C*)

2M-$HClO_4$, 2 . 10^{-3}M-HL in toluene. Curve: *1* tert-C_4H_9OH, *2* n-C_3H_7OH, *3* iso-C_3H_7OH, *4* C_2H_5OH, *5* CH_3OH.

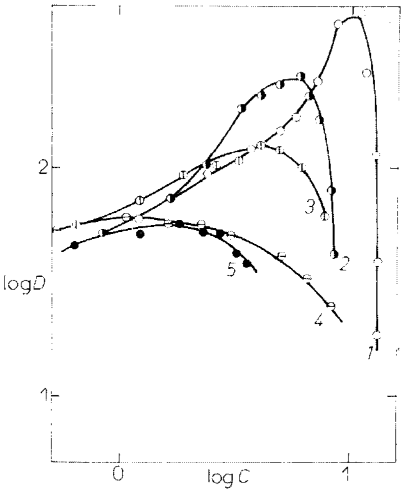


FIG. 2

Dependence of Hafnium Distribution Ratio (*D*) on the Initial Concentration of Alcohol (*C*)

2M-$HClO_4$, 4 . 10^{-3}M-HL in chloroform. Curve: *1* CH_3OH, *2* C_2H_5OH, *3* iso-C_3H_7 . . OH, *4* tert-C_4H_9OH, *5* n-C_3H_7OH

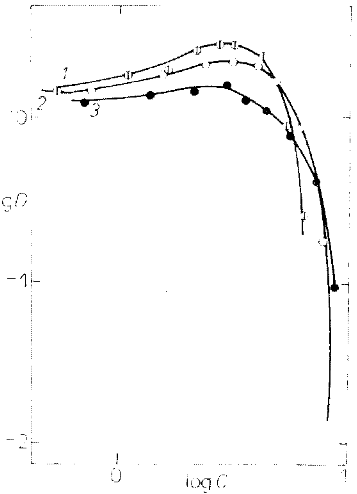


FIG. 3

Dependence of Hafnium Distribution Ratio (D) on the Initial Concentration (C) of Organic Component in the Polar Phase

2M-$HClO_4$, $1 . 10^{-3}$M-HL in benzene. Curve: *1* ethylene glycol monomethyl ether, *2* allyl alcohol, *3* propylene glycol.

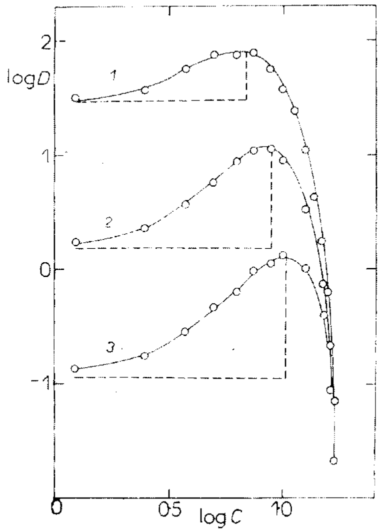


FIG. 4

Effect of Concentration of HL on the Magnitude of Synergic Effect

Aqueous–methanolic polar phase, 2M-$HClO_4$, benzene. Curve: *1* $2 . 10^{-3}$, *2* $1 . 10^{-3}$, *3* $5 . 10^{-4}$M-HL

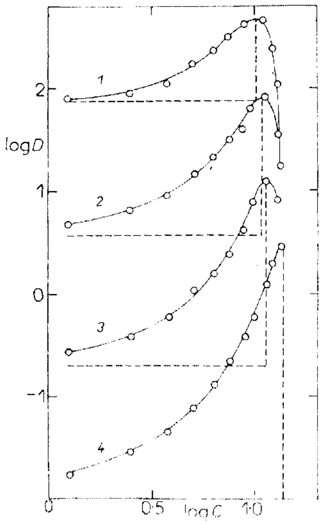


FIG. 5

Effect of Concentration of HL on the Magnitude of Synergic Effect

Aqueous–methanolic polar phase, 2M-$HClO_4$, chloroform. Curve: *1* $4 . 10^{-3}$, *2* $2 . 10^{-3}$, *3* $1 . 10^{-3}$, *4* $5 . 10^{-4}$M-HL.

The peak positions of the curves depend on the alcohol used and on the concentration of HL. At a constant HL concentration of 2. 10^{-3}M in benzene (Fig.1), toluene and CCl_4, the peaks are situated at alcohol concentrations of approximately 7M-CH_3OH, 4M-C_2H_5OH and 2·6-iso-C_3H_7OH respectively. For extractions into chloroform (Fig. 2) the peaks are situated at 10M-CH_3OH, 6·3M-C_2H_5OH and 4·9M-iso-C_3H_7OH respectively. At higher alcohol concentrations than the values mentioned

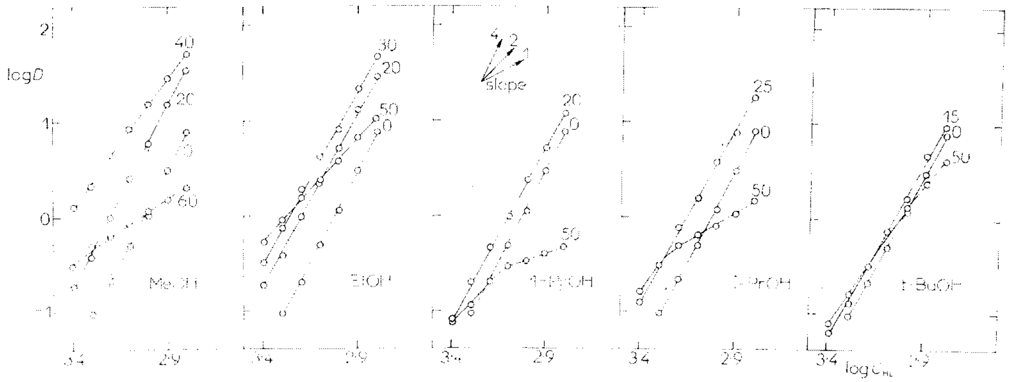


FIG. 6

Dependence of Hafnium Distribution Ratio on the Concentration of HL

Benzene, 2M-$HClO_4$. The number at each curve represents the alcohol concentration in v/v % in the polar phase (0 — extraction from aqueous 2M-$HClO_4$).

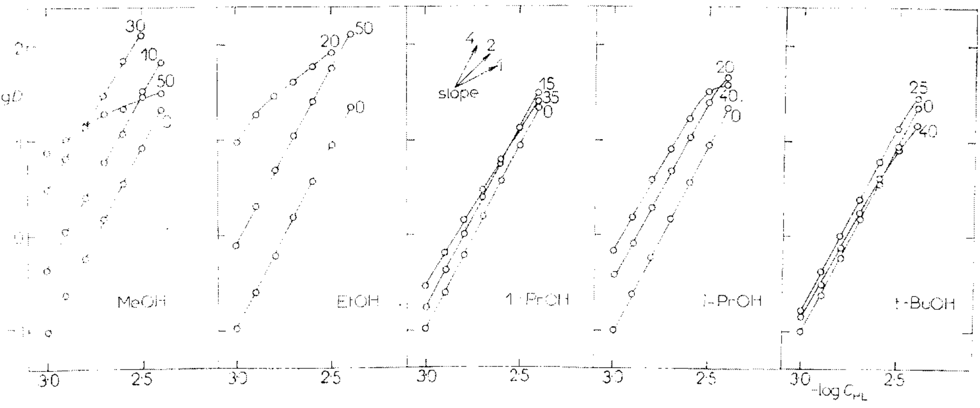


FIG. 7

Dependence of Hafnium Distribution Ratio on the Concentration of HL

Chloroform, 2 M-$HClO_4$. Curves marked identically as those in Fig. 6.

before, the values of *D* start decreasing into the region of antagonism. With the decreasing concentration of the extraction agent, on the other hand, the synergic effect is intensified and, at the same time, the peaks move toward higher concentration of alcohol. Fig. 4 and 5 show these effects for extractions into benzene and $CHCl_3$.

Dependence of D on the Concentration of HL

The title dependences for all studied alcohols are shown in Figs 6 and 7 for extractions into benzene and chloroform. Analogous plots have been found for toluene and CCl_4 (ref.[17]). In extractions from an aqueous medium or from a medium of low concentration of an alcohol, the plots are linear with the value of slope approximately 4·0 which corresponds to the extraction of the HfL_4 chelate[18]. At the higher concentration of an alcohol the value of slope decreases and in some cases the straight line becomes curved. The following slope values have been found for the plots shown in Figs 6 and 7 (of the two numbers presented, the first gives v/v% of alcohol and the second the corresponding slope value): benzene – CH_3OH: 20, 3·9; 40, 2·7; 60, 1·2; benzene – C_2H_5OH: 20 and 30, 3·8; 50, 2·1; benzene – n-C_3H_7OH: 20, 3·4; 50, 0·7; benzen – iso-C_3H_7OH: 25, 3·7; 50, 1·5; benzene – tert-C_4H_9OH: 15, 3·9; 50, 2·4; $CHCl_3$ – CH_3OH: 10, 3·9; 30, 3·7; 50, 1·2; $CHCl_3$ – C_2H_5OH: 20, 3·9; 50, 1·8; $CHCl_3$ – n-C_3H_7OH: 15, 3·8; 35, 3·6; $CHCl_3$ – iso-C_3H_7OH: 20, 3·9; 40, 3·7; $CHCl_3$ – tert-C_4H_9OH: 25, 3·9; 40, 3·7.

Distribution of HL *in the Extraction from Aqueous–Alcoholic Medium*

Fig. 8 shows the results of the spectrophotometric measurement of the distribution of HL between aqueous–alcoholic solutions and toluene. In a fairly wide interval of the concentration of alcohol, the distribution of HL is only very little affected by the presence of alcohol in the polar phase. From a certain alcohol concentration which decreases for alcohols having linear chain with the length of the chain, however, the concentration of HL in the organic phase decreases. Although the position of the synergic maximum depends on the concentration of HL (Fig. 4 and 5), there is a rough correlation between the drop in the concentration of HL and the concentration region of an alcohol where the value of *D* after having reached a maximum passes into the region of antagonism.

Relative Permittivity of Equilibrium Organic Phases

As a result of partial miscibility of a weak polar organic phase and a polar aqueous–alcoholic phase a certain amount of alcohol is transferred into the organic phase. Considering the high relative permittivity of alcohols (CH_3OH 31·5, C_2H_5OH 24·3, n-C_3H_7OH 20·1, iso-C_3H_7OH 18·3, tert-C_4H_9OH 9·9, all at 25°C, see[19]) the changes in the relative permittivity of the organic phase may be expected. The dependence of the relative permittivity of the equilibrium benzene phase on the initial concentration of alcohol is shown in Fig. 9. The relative permittivity increases, but not significantly, with the total concentration of alcohol. In the distribution of n-C_3H_7OH and tert-C_4H_9OH the organic phase becomes saturated with alchohol. The relative permittivity of equilibrium organic phase increases in the series $CH_3OH <$ $< C_2H_5OH <$ iso-$C_3H_7OH <$ n-$C_3H_7OH <$ tert-C_4H_9OH even though the relative permittivity of alcohols decreases in this series. It is caused by the sequence of solubility of alcohols in the equilibrium organic phase (see the next paragraph). The change in the relative permittivity for tetrachloromethane is even smaller (the highest being for tert-C_4H_9OH from the value 2·20 to 2·40)[17]. For chloroform (Fig. 10) the sequence of alcohol influence on the relative permittivity is the same as for solvents mentioned before but the values of the relative permittivity increase sharply for higher alcohol concentration (with the exception of CH_3OH). In addition to the higher concentration of alcohol in chloroform as compared to benzene and tetrachloromethane, this is also caused by much higher coextraction of perchloric acid (Fig. 11).

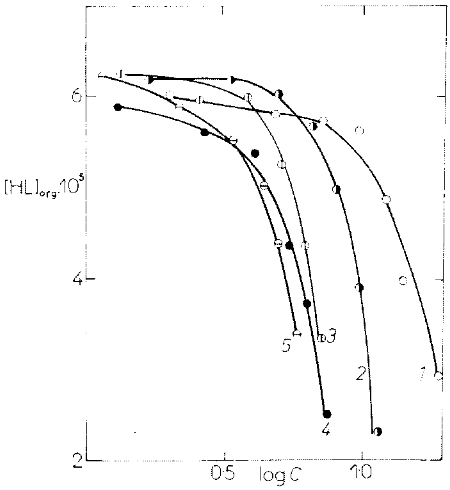


FIG. 8

Effect of the Initial Concentration of Alcohol in the Polar Phase (C) on the Distribution of HL

2M-$HClO_4$, toluene, $C_{HL,tot} = 6{\cdot}5 \cdot 10^{-5}$ M. Curves: *1* CH_3OH, *2* C_2H_5-OH, *3* iso-C_3H_7OH, *4* n-C_3H_7OH, *5* tert-C_4H_9OH.

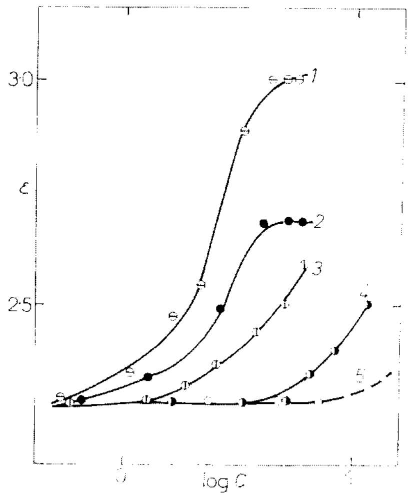
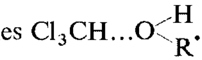


FIG. 9

Dependence of Relative Permittivity of the Benzene Phase (ε) on the Initial Concentration of Alcohol in the Polar Phase (C)

2M-$HClO_4$, Curves marked as those in Fig. 1.

Distribution of Alcohols

Results of the measurements of the distribution of CH_3OH, C_2H_5OH and n-C_3H_7OH between aqueous–alcoholic 2M-$HClO_4$ and toluene or chloroform are shown in Fig. 12 as extraction isotherms for 20°C ($[alc]_{org}$ and $[alc]_{pol}$ are equilibrium concentrations of alcohol in the organic and polar phases). The extractibility of alcohols increases with the lenght of chain and is practically the same for benzene, toluene and tetrachloromethane, and considerably higher for chloroform. This is certainly not in accordance with the continuous increase of solubility parameter in the series CCl_4 8·60, toluene 8·90, benzene 9·15, $CHCl_3$ 9·3 (see[20]). Such deviation is obviously caused by the interaction of $CHCl_3$ with alcohol in the organic phase since spectroscopic measurements[21,22] have proved the existence of molecular complexes  $Cl_3CH...O\begin{smallmatrix}H\\R\end{smallmatrix}$.

When n-C_3H_7OH is distributed between a polar phase and toluene, tetrachloromethane and less apparently also benzene[17], the organic phase gets saturated with the alcohol at $[alc]_{pol} > 5$M. This is agreement with analogous behaviour of the relative permittivity of the organic phase.

Using these measurements it is possible to convert the dependence of *D* on the total concentration of alcohol to the dependence of *D* on the equilibrium concentration of alcohol in the organic phase. This is shown in Fig. 13 for some measurements using methanol.

DISCUSSION

Synergism

Discussing extractions from mixed aqueous–alcoholic media it is first of all essential to consider the physico-chemical effects which might make the common two-phase extraction systems with a simple aqueous phase more complicated.

There are in the first place changes of the formal acidity of the aqueous–alcoholic phase which take place as a result of mutual though limited miscibility of phases. The change of *D* caused by acidity variations is given by the equation

$$\Delta \log D = n(\log [H]_{init}/[H]_{pol}),$$

where $[H]_{init}$ is the initial formal acidity (2M in all our measurements), $[H]_{pol}$ is the equilibrium formal acidity of the polar phase, and n is the slope value of the plot log *D* *vs* log $[H]_{tot}$ at the same concentration of alcohol. It has been calculated from this equation that for benzene, toluene and CCl_4 up to the concentration of alcohol 30–40 v/v%, *i.e.* in the region which takes also into account the shift of the synergic maximum with the concentration of HL (Fig. 4), the volume changes result in only a very small increase of the formal acidity of the polar phase. As a result of this, the value of D should decrease (*e.g.* $\Delta \log D \approx -0{\cdot}05$ for the system 20 to 30 v/v% n-C_3H_7OH/benzene). Although all these calculations are only very approximate (the activity of H_3O^+ ions in the aqueous–alcoholic solutions of high ionic strength is not known), it is possible to eliminate the influence of such changes on the origin of synergism. This is well manifested on systems with methanol (Figs 4 and 5) where synergism is the most pronounced and yet there are no changes in the values of $[H]_{pol}$. The identical conclusion can also be drawn for chloroform although here the theoretical decrease of D is higher ($\Delta \log D = -0{\cdot}24$). This decrease is obviously compensated by higher equilibrium concentration of alcohol in the chloroform phase (Fig. 12) and for that reason the magnitude of synergic effects does not practically differ from that for the other solvents.

Also the changes of the relative permittivity of the organic phase are probably not the decisive ones not only because they are small (Figs 9 and 10) but also that the extraction of chelates depends rather little on the relative permittivity of a solvent[23]. The changes of the relative permittivity of the polar phase in the extraction of Hf^{4+} may affect the distribution constant of the chelate and the solvation of the Hf^{4+} ion in

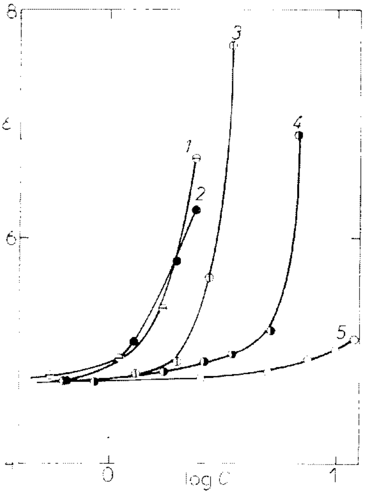


FIG. 10

Dependence of Relative Permittivity of the Chloroform Phase (ε) on the Initial Concentration of Alcohol in the Polar Phase (C) 2M-$HClO_4$.

Curves marked as those in Fig. 1.

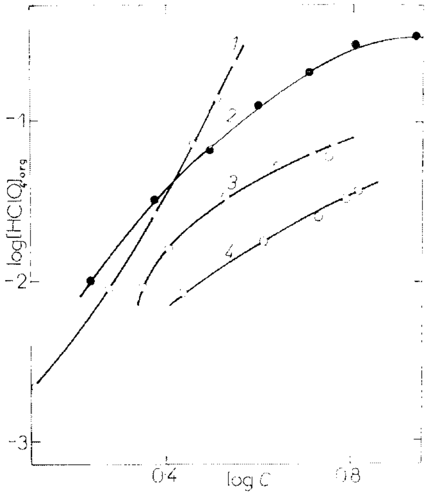


FIG. 11

Coextraction of Perchloric Acid with Alcohols into the Organic Phase

$C(HClO_4)_{tot} = 2M$. Curve: *1* n-C_3H_7.$OH/CHCl_3$, *2* tert-$C_4H_9OH/CHCl_3$, *3* tert-C_4H_9OH/benzene, *4* n-C_3H_7OH/benzene.

that phase. The distribution constant of the chelate, however, changes analogously with that of the chelating agent[23] and it is obvious from Fig. 8 that there is no change in the distribution constant of HL in the region of synergism. For the same reason, the effect of the relative permittivity of the organic phase on the distribution constant of the chelate may also be ruled out. However, changes of the solvation of the Hf^{4+} ion in the polar phase with the increasing concentration of alcohol cannot be so simply excluded. The comparison with other chelating agents[17] (*e.g.* there is no synergism for 2-theonyl-trifluoroacetone in the presence of alcohols) indicates that this effect is not likely to be predominat because if it was, the magnitude of the synergic effect would not depend so much on the type of extracting agent.

The increase of the extractibility is probably caused by the formation of an adduct (solvate) of the HfL_4 chelate with alcohol molecules in the organic phase. Based on the observations which have been carried out, the only definite assumption about the adduct structure is that it keeps the original ratio of components of the HfL_4 chelate. This is proved by the plots log D *vs* log $[HL]_{tot}$ (Figs 6 and 7), slopes of which are very close to the value of 4·0 in the region of the synergic maximum. The number of alcohol molecules in the adduct could not be determined because the logarithmic

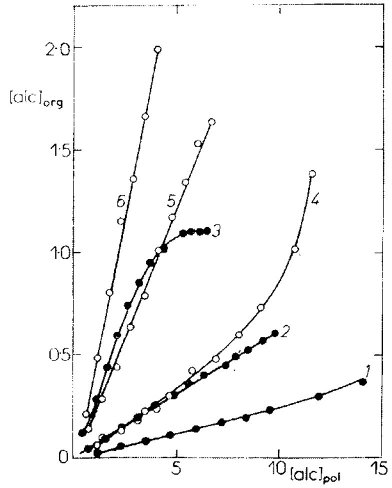


FIG. 12

Extraction Isotherms of Alcohols

2M-HClO$_4$. Curve: *1*—*3* toluene, *4*—*6* chloroform; *1* and *4* CH_3OH, *2* and *5* C_2H_5. .OH, *3* and *6* n-C_3H_7OH.

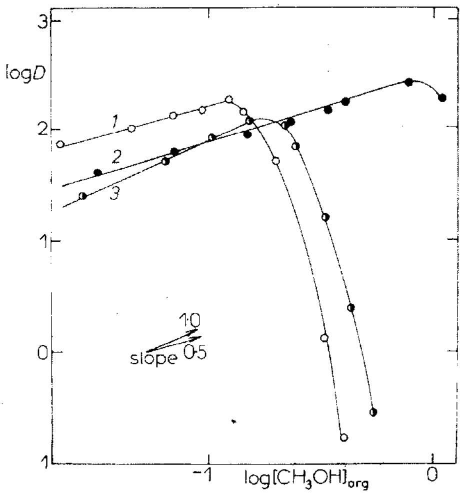


FIG. 13

Dependence of Hafnium Distribution Ratio (D) on the Equilibrium Concentration of Methanol in the Organic Phase

2M-HClO$_4$. Curve: *1* 2 . 10^{-3}M-HL in CCl_4. *2* 4 . 10^{-3}M-HL in $CHCl_3$, *3* 2 . 10^{-3} M-HL in benzene.

plots of *D* on the equilibrium concentration of alcohol in the organic phase (Fig. 13) have different slope values for different but constant concentrations of HL since the synergic increase of *D* is a function of that concentration (Figs 4 and 5). It seems therefore obvious that the value of slope close to 1·0 for the case of HL in benzene is just incidental and cannot be interpreted as the solvation number. Other factors which make the whole picture more complicated are the association equilibria of alcohols in organic solvents[24-26], which in a two-phase system are further complicated by the hydration of alcohols in the organic phase[17].

Since the coordination number of hafnium higher than 8 can hardly be expected[27], the basic centres of the HfL_4 chelate are probably solvated by alcohol molecules by means of hydrogen bonds. The formation of solvates of acetylacetonates of such kind has been described in several papers. Monohydrated acetylacetonates of erbium and dysprosium, for example, form disolvates with methanol and the energy of the chelate – CH_3OH bond was estimated from the temperature function of the vapour pressure as 6·6 kcal/mol. This value corresponds to a relatively strong hydrogen bond or to a dipole-dipole interaction[28]. The existence of a monosolvate of thorium acetylacetonate with methanol was confirmed by infrared spectra[29]. Also the heat of dissolution of cobalt acetylacetonate in mixtures of alcohols with CCl_4 confirms the solvation of this coordination-saturated chelate[30]. Some other observations are also in accordance with the above explanation of synergism. It is firstly the fact that when alcohol in the polar phase is replaced by a solvent not containing the hydroxyl group (acetone, dimethyl sulphoxide, tetrahydrofurane, acetonitrile) the synergism does not occur. The second fact is that the HfL_4 chelate, which precipitates at the interphase when macroconcentrations of hafnium (0·06M-Hf(IV) + 0·2M-HL) are

TABLE I

Coextraction of Alcohols with HL into Benzene in the Presence of 20 v/v % Alcohol

Organic phase	$[CH_3OH]_{org}$	$[C_2H_5OH]_{org}$ mol l^{-1}	$[n\text{-}C_3H_7OH]_{org}$
Benzene	0·12	0·26	0·51
0·1M-HL in benzene	0·15	0·29	0·68
0·1M-HL in the form of HfL_4 chelate in benzene[a]	0·15	0·29	0·68

[a] The used concentrations —0·06M-Hf (IV) and 0·1M-HL assure that practically all HL in the organic phase is complexed in the chelate.

extracted into benzene, dissolves after alcohol has been added and the mixture agitated for a few hours.

Also the synergic efficiency of alcohols agrees with the suggested formation of a solvate. Although the height of the synergic maximum decreases with increasing length of chain, one can see from Figs 1 and 2 that C_2H_5OH causes synergism at lower concentration than CH_3OH. Since with the increasing length of chain of alcohol the alcohol concentration causing the reduction of the distribution ratio of HL (Fig. 8) decreases, both phenomena compete with the result in the observed series of heights of synergic maxima. This effect is especially evident for n-C_3H_7OH where synergism is practically completely suppressed.

Antagonism

At higher concentrations of the organic component in the polar phase, the value of *D* starts to decrease (Figs 1, 2, 4, 5). The region of this decrease also depends on the concentration of HL. The comparison of curves in Fig. 1 with the distribution of HL (Fig. 8) shows an evident relation of both phenomena because the regions of both the destruction of synergism and the decrease of the distribution ratio of HL coincide. The increase of the HL concentration in the polar phase results also in the increased degree of complexation of hafnium in that phase and is the reason of the reduction in slope values of the plots log *D* *vs* log $[HL]_{tot}$ at higher concentrations of alcohol (Fig. 6 and 7). After correction of *D* for the change of HL concentration, the obtained curves are analogous to those which had not been corrected, only the region of the decrease of *D* is shifted toward higher concentration of alcohol. This proves that the increased solubility of HL in the polar phase at higher alcohol concentrations is not the only reason for the destruction of synergism to which obviously the interaction of HL with alcohol also contributes. This is indicated by higher extraction into benzene of alcohols in the presence of 0·1M-HL as compared with pure benzene (Table I). The concentration ratio of HL to alcohol in the equilibrium benzene phase is ≈ 3 for CH_3OH and C_2H_5OH and $\approx 0{\cdot}6$ for n-C_3H_7OH. It is interesting from the point of view of synergism that using HL in the form of the chelate (prepared under the condition of quantitative substoichiometric extraction) the same amount of alcohol is coextracted as with free HL. This indicates that the alcohol-HL and alcohol–hafnium chelate interactions are of the same type. It also favours the proposed concept of synergism *via* solvation of basic centres of coordinated ligands in the chelate.

Volume changes are the further cause of antagonism in case of n-C_3H_7OH, iso-C_3H_7OH and tert-C_4H_9OH. In systems containing benzene, toluene or CCl_4 and in the concentration region 10–30 v/v% alcohol in the polar phase, swelling of the organic phase occurs which results in the decrease of $[HL]_{org}$ and the reduction of the hafnium extraction.

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