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Original Scientific Paper

Formation of Metal Complexes with the Arsenazo I and Arsenazo III Reagents as Functions of the Medium Acidity*

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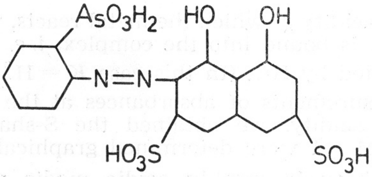
A function is given for the medium acidity in which metals react with arsenazo I and arsenazo III, as dependent upon the solubility product of the metal hydroxides. For each reagent a linear function is found:

$$-\log H_{1/2} = a\,(pK_s) + b$$

A study has been made on the protonation of the arsenazo I reagent. Binding of the metal and the proton with arsenazo I is discussed and found that it is anologous to that of arsenazo III[11,12].

INTRODUCTION

The arsenazo type reagents: arsenazo I — [2 — (*o*-arsonophenyl-azo)1 : 8-dihydroxy-naphthalene-3 : 6-disulphonic acid trisodium salt and arsenazo III 2 : 7-bis-(*o*-arsonophenyl-azo)-1 : 8-dihydroxy-naphthalene-3 : 6-disulphonic acid sodium salt are used nowadays for the spectrophotometric determination of several elements, such as Th, Zr, U, Sc, rare earths and transuranium elements[1–5].



ARSENAZO I

V. I. Kuznetsov[1–5] suggested that arsenazo I was the reagent for Th, U and rare earths. S. B. Savvin[6] have prepared arsenazo III and applied it to the spectrophotometric determination of U, Th, Zr, Sc, rare earths and some other elements[2, 3, 7, 13].

Both reagents are at present widely used, especially arsenazo III, which gives more stable complexes and reacts with Zr, Th and U even in strongly acidic media[3, 4, 6, 7].

Towards the beginning of the investigation of the arsenazo reagents, V. I. Kuznetsov[9] pointed out that the effect of these reagents (type R-OH) might be considered as a process analogous to the process of hydrolysis. Metal complexes are formed in more acidic media if the metal hydrolyzes at lower *p*H values.

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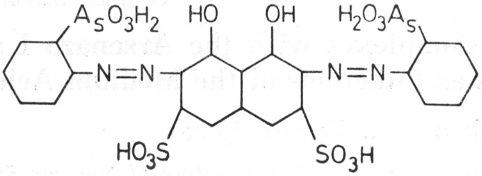
A. A. Nemodruk[8] emphasized the dependence of the reaction of arsenazo III with metals on the ratio of the atomic number and the ionic radius of the metal (Z/r). If Z/r is smaller than or equal to 39, the metals give blue or violet complexes, and for Z/r greater than or equal to 46, the complexes are green.



ARSENAZO III

In this paper, we wished to find a mathematical expression for the function of the medium acidity at which a metal reacts with the reagent, as dependent upon the solubility product of the metal hydroxide (pK_s). A large part of the paper deals with the arsenazo III reagent, whereas the arsenazo I reagent was investigated to make the conclusions on the principles concerning arsenazo III more complete.

EXPERIMENTAL

The formation of the complexes was examined as a function of the medium acidity with samples where the metal concentration was constant and the reagent concentration in a constant excess, so that in the equation

$$M + (a + n)\,RH \overset{K}{\rightleftarrows} MR_n + n\,H + a\,RH$$

$a \gg n$ could be assumed, the equilibrium constant then being given by

$$K = \frac{MR_n}{M} \times H^n$$

In characterizing the medium acidity at which the metal reacts, we took the H-ion activity at which 50% of the metal is bound into the complex, *i. e.* $MR_n/M = 1$. This value of the H-ion activity is denoted by $H_{1/2}$. (In this case $K = H^n_{1/2}$).

From spectrophotometric measurements of absorbances at the complex absorption maximum as a function of acidity, we obtained the S-shaped curves $A = f(-\log H)$. The values of $MR_n/M = 1$ were determined graphically.

The value of the H-ion activity in weakly acidic media was obtained by measuring the *p*H of the solution, while for strongly acidic solutions (above 1 *N*) of perchloric and sulfuric acids, we used the values of Hammett's functions[10].

The $H_{1/2}$ value for the arsenazo III-zirconium complex and the protonation value of arsenazo III were taken from our previous works[11,12]. Repeated experiments for the La- and Sc-arsenazo III complexes were in good agreement with the earlier results[13]. In this paper, the values of $H_{1/2}$ for complexes of Th and U with arsenazo III were determined and also for complexes of Th, La and Zr with arsenazo I.

The experimental data and the function of $-\log H_{1/2}$ on the pK_s for metal complexes formed with arsenazo I indicated the possibility of protonation of arsenazo I in strongly acidic media ($H_0 \sim -6$), so that we investigated the protonation and determined the protonation constant.

Function of — log $H_{1/2}$ and pK_s for Metal Complexes with Arsenazo III

The function of the absorbance of the complex and the acidity for Th, U, Sc, La, Zr is given in Fig. 1. The metal concentration is 4×10^{-6} *M*, and the ratio $M : R = 1 : 10$.

Table I gives the values of $-\log H_{1/2}$ for individual metal complexes with arsenazo III as well as the values of the solubility product of the metal hydroxides $(pK_s)^{14}$.

Function of $-\log H_{1/2}$ and pK_s for metal complexes with arsenazo III are shown in curve A in Fig. 3.

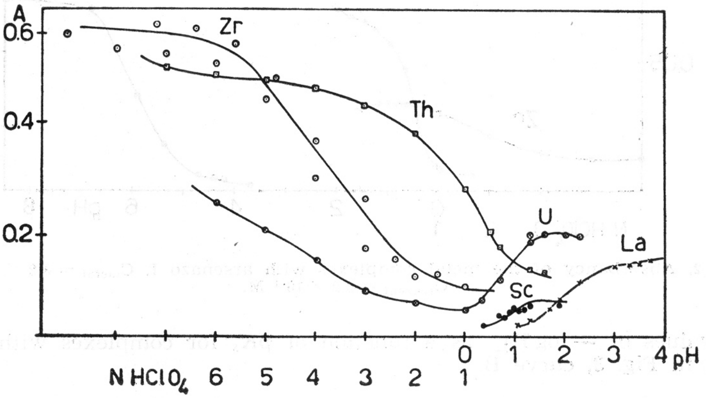


Fig. 1. Absorbancy of the metal complexes with arsenazo III. $C_{metal} = 4 \times 10^{-6}$ M $C_{reagent} = 4 \times 10^{-5}$ M.

TABLE I

Values of $-\log H_{1/2}$ *for the metal complexes with arsenazo III and solubility product of the metal hydroxides* (pK_S).

Metal	$-\log H_{1/2}$	pK_S^{14}
La^{3+}	1.95	18.7
Lu^{3+}	2.20	23.7
Y^{3+}	2.08	22.1
Sc^{3+}	0.80	30.1
UO_2^{2+}	0.85	21.9
	-0.75	
Th^{4+}	-0.10	44.4
Zr^{4+}	-1.20	52.0
H^+	-5.04	

Function of $-\log H_{1/2}$ *and* pK_s *for Metal Complexes with Arsenazo I*

To find whether similar function as for arsenazo III exists for $-\log H_{1/2}$ and pK_S for arsenazo I, we determined $H_{1/2}$ for Th, Zr and La complexes with arsenazo I. The results are shown in Table II and in Fig. 2.

TABLE II

Values of $-\log H_{1/2}$ *of the metal complexes with arsenazo I, and the solubility product of the metal hydroxides* (pK_S).

Metal	$-\log H_{1/2}$	pK_S^{14}
La^{3+}	6.10	18.7
Th^{4+}	0.50	44.4
Zr^{4+}	-0.25	52.0

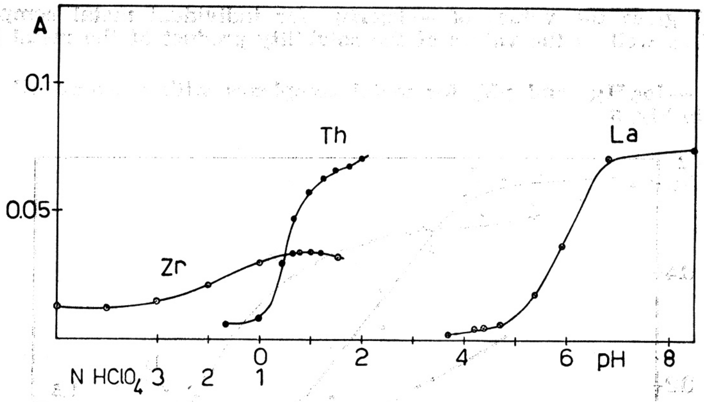


Fig. 2. Absorbancy of the metal complexes with arsenazo I. $C_{metal} = 3.2 \times 10^{-5}$ *M* $C_{reagent} = 3.2 \times 10^{-4}$ *M*.

The values of $-\log H_{1/2}$ as a function of pK_s for complexes with arsenazo I are shown in Fig. 3, curve B.

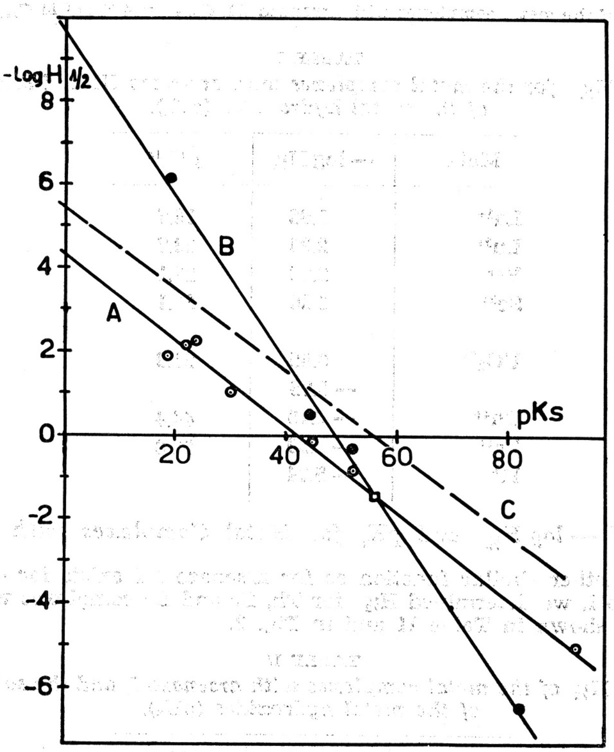


Fig. 3. Functions of $-\log H_{1/2}$ and pK_s for metal complexes: with arsenazo III (curve A), with arsenazo I (curve B). Curve C is the difference between A and B curve.

Since the protonation constant for arsenazo III has the value of $-\log H_{1/2} = 5.04$[11] and corresponds to an abscissa at about pK_s 85, we supposed that the protonation of arsenazo I should also take place at the same value of the abscissa (about 85) in curve B (Fig. 3). The ordinate of this point on curve B is about —6 (— log $H_{1/2}$). Such a high value of Hammett's function may be achieved only in solutions of concentrated sulfuric acid. Concentrated perchloric acid (70%) has the value of $H_0 = -5.5$[10].

Protonation of Arsenazo I

The arsenazo I spectrum in concentrated sulfuric acid (34 *N*) essentially differs from the spectrum in less acidic solutions. The maximum absorption in 34 *N* sulfuric acid occurs at 587 mμ (Fig. 4) and the form of the spectrum is similar to those of metal complexes with arsenazo I. The spectrum in concentrated acid is the result of the protonated form of arsenazo I, analogous to the protonated form of arsenazo III[11], and we followed the change in absorbance at 590 mμ as a function of acidity (Fig. 5).

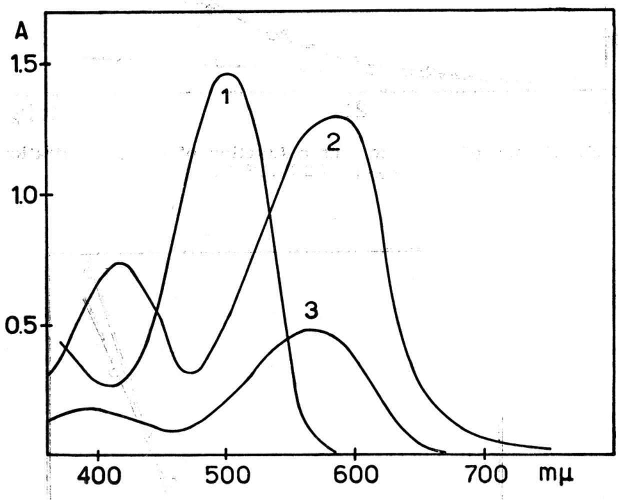


Fig. 4. Absorption spectra of arsenazo I and complex with Th.
1. Arsenazo I 8 × 10^{-5} *M* in 1 *N* H_2SO_4.
2. Arsenazo I 8 × 10^{-5} *M* in 32 *N* H_2SO_4.
3. Th complex. $C_{Th} = 3.2 \times 10^{-4}$ *M*, $C_{Az\ I} = 3.2 \times 10^{-5}$ *M*. *pH* 1.2.

The protonation of arsenazo I is expressed by the protonation constant (*K*) in the form:

$$\log \frac{H_nB}{B} = -n H_0 + \log K$$

where: B = the concentration of the non-protonated form
H_nB = the concentration of the protonated form
H_0 = Hammett's function
n = the number of protons

The molar absorptivity of the protonated form of arsenazo I (H_nB) at 590 mμ was calculated from the absorbance of the sample in 34 *N* sulfuric acid and from the concentration of arsenazo I in the sample

$$\varepsilon^{590}_{HB} = 2.62 \times 10^4$$

We neglected the molar absorptivity of the non-protonated form (B) at that wavelength, since its value was less than 10^3.

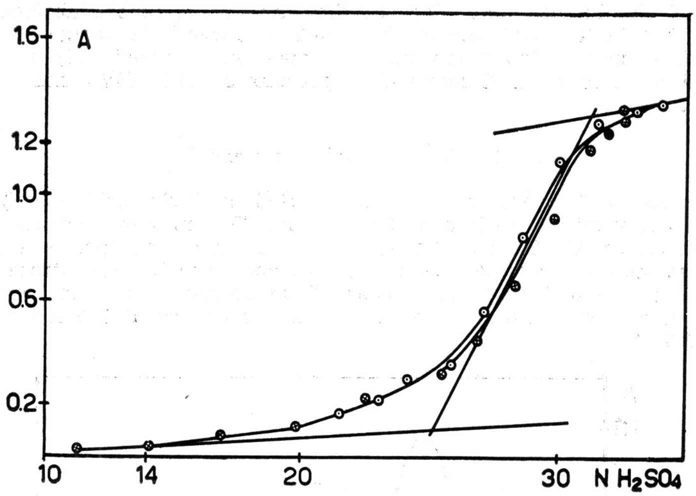


Fig. 5. Change of absorbancy of arsenazo I as a function of the concentration of sulfuric acid. $C_{Az\ I} = 5.2 \times 10^{-5}$ *M*.

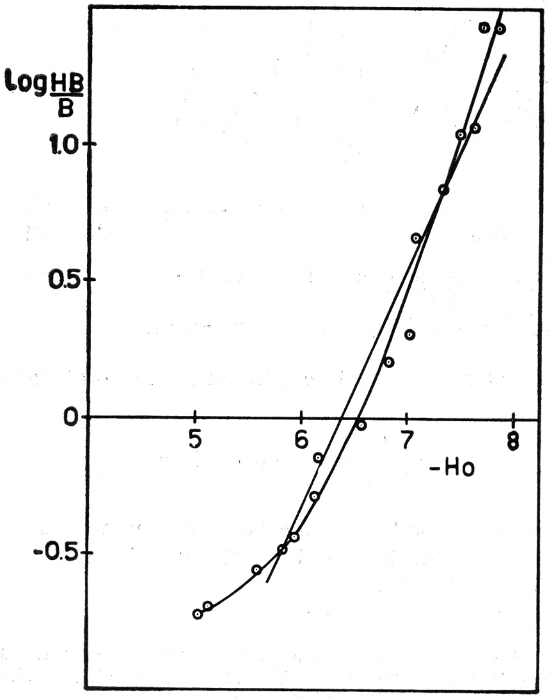


Fig. 6. Function of log HB/B on H_0 in sulfuric acid for arsenazo I. $C_{AZ\ I} = 3.2 \times 10^{-5}$ *M*.

The values of Ho for sulfuric acid were taken from the literature[10].

Figure 6 shows a plot of $\log H_nB/B$ against H_0. It may be seen that $n = 1$. The

H_nB/B ratio was calculated from the S-shaped curve and we obtained the average value of the protonation constant.

$$\log K = -(6.36 \pm 0.06)$$

Figure 6 shows that the values of $\log HB/B$ deviate from the straight line at low acidities.

The experiments show that arsenazo I also protonates at high H-ion concentrations, protonation beginning at 22—25 *N* H_2SO_4. This quality of arsenazo I has not been observed thus far[8].

DISCUSSION AND RESULTS

On the basis of our experiments it may be concluded that there is a linear function of $-\log H_{1/2}$ and pK_s for metal complexes with arsenazo I (Fig. 3, curve B), and arsenazo III (Fig. 3, curve A).

If the results for complexes with arsenazo III (Table I) and complexes with arsenazo I (Table II) are interpreted with the least squares method, we obtain a linear function as follows:

for arsenazo III: $-\log H_{1/2} = -0.101\, pK_s + 4.2$*

for arsenazo I: $-\log H_{1/2} = -0.198\, pK_s + 9.7$

The medium acidity in which the metal reacts with a R-OH type reagent is a function of the solubility product of the metal hydroxide. For arsenazo I and arsenazo III functions of the general form:

$$-\log H_{1/2} = a\, pK_s + b$$

are found.

These linear functions confirm the empirical observations of V. I. Kuznetsov[9] concerning the dependence between the order of metal reaction and its hydrolysis.

One may notice that the difference $\Delta(-\log H_{1/2})$ between any two elements for the same reagent is greater in arsenazo I than in arsenazo III. It should be pointed out that Th and Zr react with arsenazo III in strongly acidic media. This is seen from the S-shaped curves (Fig. 1) which are, for Th and Zr, of »inverse« form, *i. e.* the complex is formed with increasing acidity. In the case of arsenazo I, Th and Zr complexes are formed with decreasing acidity (Fig. 2).

The values of the protonation constant ($K = H_{1/2}$) for arsenazo I and arsenazo III gave the abscissa at 82.2 and 91.9 respectively. Since the abscissa of $-\log H_{1/2}$ of the metal complex is the pK_s of the metal, the abscissa at pK_s 85 corresponds to the process analogous to the protonation of the reagent. In our opinion, it should be the process of binding protons from the dissociated acid to the water molecules:

$$HA \rightleftarrows H^+ + A^-$$

$$H^+ + n\, H_2O \rightleftarrows H^+(H_2O)_n$$

and pK_s value of about 85 would correspond to the constant

$$K = H \times (H_2O)^n$$

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* The standard deviation of the slope is 0.007, and 0.2 for the intercept.

Similar to the earlier observation for the abscissa corresponding to reagent protonation, the ordinates of the abscissa $pK_s = 14$ should correspond to dissociation of the OH groups of the arsono groups because the binding of the metal into a complex occurs because of it. The values for the dissociation constants of these groups taken from the literature are as follows:

for arsenazo III[15] $K_3 = 3.9 \times 10^{-3}$, $K_4 = 3.9 \times 10^{-3}$
$K_5 = 5.6 \times 10^{-6}$, $K_6 = 5.6 \times 10^{-6}$
for arsenazo I[16] $K_3 = 2 \times 10^{-3}$, $K_4 = 2 \times 10^{-8}$

If the pK values are taken for the first dissociation constant of the arsono group, this value is low and deviates from straight line, while the last pK value of the arsono group is high.

The value of $-\log H_{1/2}$ for the arsenazo III complex with uranium does not correspond to the abscissa pK_s for the solubility product of uranyl hydroxide, which supports the assumptions[4,8] that not uranyl ion, but another form, most probably UO^{4+} reacts with arsenazo III.

From the linear function of $-\log H_{1/2}$ for arsenazo I and arsenazo III the function of the difference can be found (Fig. 3, curve C)

$$\log H_{1/2}^{III} - \log H_{1/2}^{I} = -0.097\ pK_s + 5.4$$

where $\log H_{1/2}^{I}$ and $\log H_{1/2}^{III}$ refer to arsenazo I and arsenazo III respectively.

The difference is again a linear function of pK_s, from which it may be noticed that its value is positive up to $pK_s = 55.9$, and than it becomes negative. This confirms the experimental facts illustrating that metals with arsenazo III react in more acidic medium than with arsenazo I, while arsenazo I protonates in more acidic medium than does arsenazo III ($pK_s > 55.9$).

Binding of metals into complex with arsenazo III and protonation of arsenazo III has been discussed a number of times[2, 3, 7, 8, 11, 12] and it may be taken that this problem is, to some extent, clear[11, 12].

Our experiments with arsenazo I, especially protonation of arsenazo I, indicate that the binding of metals in complexes with arsenazo I should be explained in a similar manner as in the case of arsenazo III.

Arsenazo I protonates in strongly acidic medium. The difference $\Delta\lambda$ between the maximum of the protonated and non-protonated form is 82 mμ. A similar shifting of the absorption maximum in the protonation of arsenazo III amounts to 129 mμ[11]. This may be explained by the formation of a π-hydrogen bond of proton with a molecule of arsenazo I over the nitrogen of diazo group. This bond changes the electron charge in the π-system of the reagent molecules and the resulting shift of the maximum is 87 mμ. The shift is smaller than in arsenazo III owing to the arsenazo I structure itself.

The absorption spectra of metal complexes formed with arsenazo I are similar to the spectra of the protonated arsenazo I form; hence the bonding of metals with arsenazo I would be similar to proton bonding. Contrary to the assumption of A. A. Nemodruk[8], that in arsenazo I metals substitute the H atom of the arsono group without entering the conjugated double bond system, our results support the bonding of metals, as well as H-atom, over the six-membered ring, changing π-electron charge of the whole system in the same way as in complexing with arsenazo III[7, 8, 11, 13, 17,18].

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IZVOD

Formiranje kompleksa metala sa reagensima arsenazo I i arsenazo III u funkciji kiselosti sredine

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Data je zavisnost između kiselosti sredine u kojoj metal reaguje sa reagensima arsenazo I i arsenazo III i proizvoda rastvorljivosti hidroksida tog elementa. Za svaki reagens utvrđena je linearna zavisnost

$$-\log H_{1/2} = a\,pKs + b$$

Proučena je protonizacija reagensa arsenazo I. Diskutovano je o načinu vezivanja metala i protona u kompleksu sa arsenazo I i zaključeno je da je ono analogno kao i kod arsenazo III[11,12].

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