

STUDIES ON FLUORIDE-ZIRCONIUM ALIZARIN RED S REACTION

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ABSTRACT: The stoichiometry of Zirconium-Alizarin red S (Zr-ARS) was determined by different spectrophotometric methods (molar ratio, straight line, continuous variation, slope ratio and limiting logarithmic) at $\lambda=520$ nm. The stoichiometry of (Zr-ARS) complex was 1:1. The pK values were obtained. The straight-line method for Zr-ARS-F complex reaction pointing to the formation of 1:1:1 species. The latter reaction was affected by different factors such as acidity, temperature, time, the content of the blank and the constituents of synthetic seawater. The kinetics of the formation Zr-ARS complex was studied at different temperatures and variable fluoride concentrations. The rate constant, the energy of activation (E_a) and the enthalpy (ΔH) values were calculated.

Zr-ARS lake is formed from the reaction of Zr^{IV} and ARS. The reagent is of reddish violet colour and it is used in the determination of fluoride concentration in seawater and drinking water. However, in the presence of an acid the reddish violet colour is destroyed. The fluoride content is measured by detecting the bleaching of this lake^(1,2). The Zr-ARS reagent containing sulphuric acid is used to lessen the interference of sulphate ion in water, which is one of the most active interfering substances in the fluoride determination. The lakes are formed with a molar ratio of Zr:ARS of 1:1, regardless of whether they were formed from equivalent amounts of Zr^{IV} and ARS or with one of them excess^(3,4). If zirconium is in excess with Zr-ARS ratio in the presence of sulphuric acid, most of the Zr^{IV} excess would be complexed with SO_4^{2-} forming $ZrSO_4^{2+}$, $Zr(SO_4)_2$ and $Zr(SO_4)_3^{2-}$ ⁽⁵⁾. The addition of 25% extra $ZrO(NO_3)_2$ lessened the sensitivity of the fluoride and result in greater fluctuations with sulphate. But the addition of 25% extra ARS to the normal indicator gave a slightly greater sensitivity to fluoride and moderate sulphate concentration with considerable loss of linearity of fluoride response⁽⁶⁾.

Zr salts form with ARS a red complex in presence of 1 M- $HClO_4$ and acetone. Maximum intensity is attained within 30 minutes, F^- and PO_4^{3-} interfere⁽⁷⁾. During complexation, the $Zr(OH)_2^+$ species is the predominate. The reaction of alizarin blue S in 0.5 N HCl and 10% acetone with Zr salts gives blue 1:1 and 1:2 complexes⁽⁸⁾. The specific red colour formed between alizarin complexone (3-amino-methyl alizarin-N,N-diacetic acid) and some lanthanides is converted to a blue ternary complex in the presence of fluoride. The use of lanthanum chelate in the presence of acetone gave a much more stable colour⁽⁹⁾.

The aim of work is to study the stoichiometry, stability constants and kinetics of Zr-ARS reaction under different temperatures and variable fluoride concentrations. The optimum factors that affect Zr-ARS reactions aided the determination of F^- concentration in natural waters.

Experimental

The fluoride concentration was determined using the procedure of Zr-ARS⁽⁶⁾, with slight modifications. Standard fluoride solutions (10 $\mu gF^-/ml$) were prepared. The optimum time of measuring was two hours after mixing the components. $ZrCl_4$ solution was prepared and standardized complexometrically⁽¹⁰⁾. The absorbance was measured at $\lambda=420$ and 520 nm using Berkin Elmer Lambda 1 UV/Visible single beam and Shimadzu double-beam UV-150-02 spectrophotometers. Synthetic seawater with $Cl\%=19.00$ was prepared following Lyman and Fleming procedure⁽¹¹⁾.

Results and discussion

1- The determination of the stoichiometry of Zr-ARS complex: Different methods were used.

a) Molar ratio method⁽¹²⁾:

For the reaction: $Zr + n H_2L \leftrightarrow Zr(H_2L)_n$
(n = the number of ligands coordinated to Zr^{IV})
If the concentration of Zr^{IV} is kept constant at 1.468×10^{-4} M, while that of ARS was varied between 3.2×10^{-5} and 4.8×10^{-4} M, the absorbance (A) of Zr-ARS was measured at $\lambda=520$ nm:

$$A = \epsilon [Zr(H_2L)_n] l$$

Assuming that Beer's Law is obeyed, where ϵ being the molar extinction, l the thickness of the cell in centimeter and the brackets refer to the equilibrium concentration of the complex. The species traced with 1:1 a stoichiometry, Figure (1). If the concentration of Zr-ARS is C, its absorbance would be the same as

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the absorbance A_m which is the limiting absorbance that only reached when large excess of the ligand exists in the solution. Actually, the formation of the complex is not quite complete at the end point and so, the absorbance A at the end point is smaller than A_m . The dissociation constant K of Zr-ARS complex is calculated using the equation:

$$K = \frac{C \left(1 - \frac{A}{A_m}\right)^2}{\frac{A}{A_m}}$$

Where, $K = 1.498 \times 10^{-6}$, $pK = 5.82$

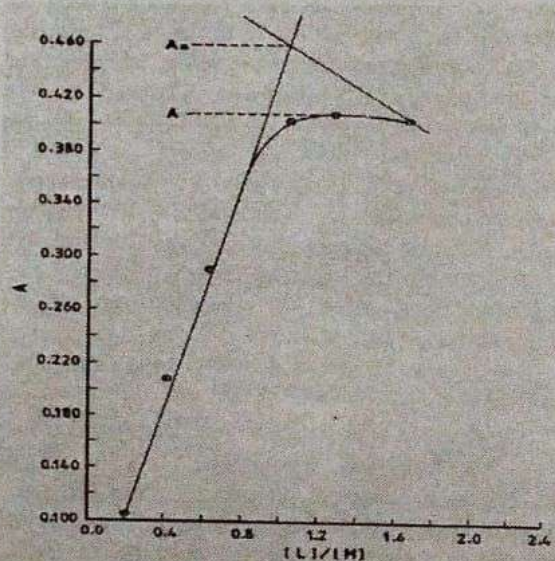


Figure (1): Molar ratio method.
[Zr^{IV}] = 1.468×10^{-4} M; Blank = ARS; $\lambda = 520$ nm.

b) Straight line method:

From the path of the absorbance concentration curve⁽¹³⁾:

$A = f(V)$, where A is the absorbance of the coloured solution and V is the volume of the reagent ARS. Figure (2), represents the simple plot relation between $(1/A)$ versus $(1/v)^n$, where (v) is the volume of the added ARS with respect to 1 ml of 0.00367 M of Zr^{IV}. A best-fit straight line is obtained with $n=1$ to suggest the presence of 1:1 stoichiometry.

On plotting $\log A$ versus $\log v$, a straight line is obtained from which (n) and $\log (CD/K)$ values are derived from the slope and the intercept, respectively (Figure 3).

$$\log A = \log (CD/K) + n \log v$$

$$C = (a_0 v_0/V) \epsilon = 0.4139; D = (b_0/V)^n = 1.6 \times 10^{-4}$$

V = the volume of the measuring flask.

b_0 = the concentration of ARS.

n = the slope of the straight line

K = the equilibrium constant of Zr-ARS complex.

a_0 = the concentration of Zr^{IV}.

v_0 = the volume of Zr^{IV}.

ϵ = the molar extinction coefficient = 2820.

$n = 0.84$, where, $K = 6.018 \times 10^{-5}$; $pK = 4.221$

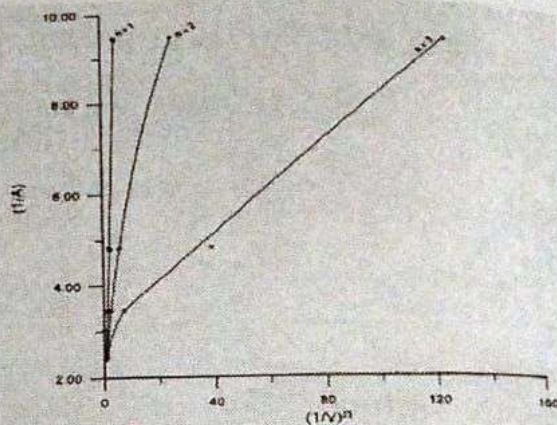


Figure (2): Straight line method (simple plot)
[Zr^{IV}] = 1.468×10^{-4} M; Blank = ARS; $\lambda = 520$ nm.

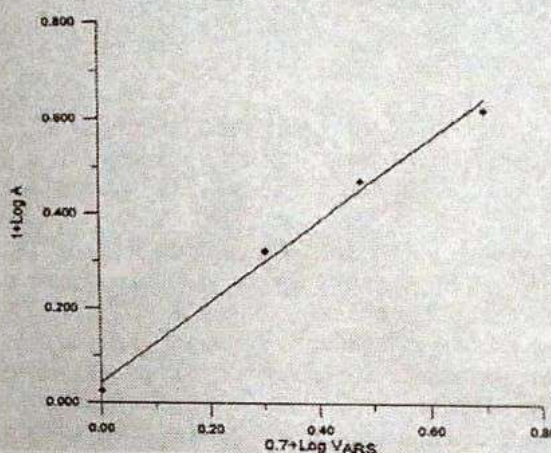


Figure (3): Straight line method (Logarithmic plot).
[Zr^{IV}] = 1.468×10^{-4} M; Blank = ARS; $\lambda = 520$ nm.

c) Continuous variation method⁽¹²⁾:

Plotting the absorbance against the mole fraction of Zr^{IV}, when the concentration of ZrCl₄ is (0.00367 M) and that of ARS is (0.004 M) in 25 ml measuring flask at 520 nm, gave a peak at $n = 0.565$ with 1:1 stoichiometry, Figure 4. The deduced equation given for the 1:2 complex is applied, where $K = 2.36 \times 10^{-6}$; $pK = 5.63$

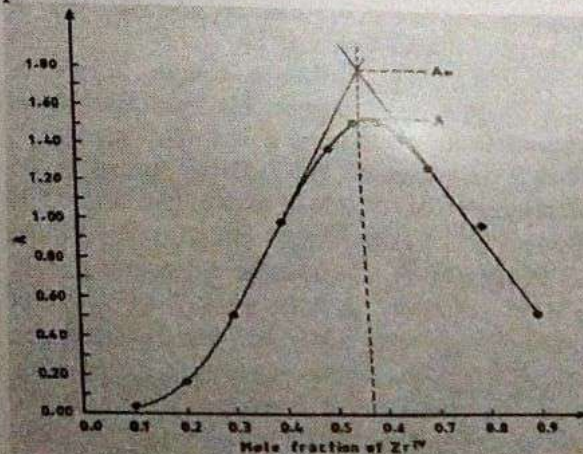


Figure (4): Continuous variation method: A - mol fraction of Zr^{IV} relation
[Zr^{IV}] = 0.00367 M; [ARS] = 0.004 M; Blank = ARS;
 $\lambda = 520$ nm.

d) Slope ratio method⁽¹⁴⁾:

In the reaction: $m \text{Zr}^{\text{IV}} + n \text{H}_2\text{L} \leftrightarrow [(\text{Zr})_m(\text{H}_2\text{L})_n]$
 Where, (m) denotes the number of Zr^{IV} moles, (n) the number of moles of ARS (H_2L). $[(\text{Zr})_m(\text{H}_2\text{L})_n]$ represents the Zr-ARS complex. If the concentration of ARS is kept constant ($8 \times 10^{-4} \text{ M}$) and in sufficient excess to make dissociation negligible, the equilibrium concentration of $[(\text{Zr})_m(\text{H}_2\text{L})_n]$ will be essentially proportional to the analytical concentration of Zr^{IV} added in the reaction:

$$[(\text{Zr})_m(\text{H}_2\text{L})_n] = \frac{C_{\text{Zr}^{\text{IV}}}}{m}$$

The brackets refer to the equilibrium concentration of Zr^{IV} .

If absorbance (A) is plotted against different analytical concentrations of Zr^{IV} keeping the concentration of H_2L constant and in excess, a straight line is obtained with a slope_I = $\epsilon l/m$.

Similarly, if the concentration of Zr^{IV} is kept constant ($7.8 \times 10^{-4} \text{ M}$) in excess and the concentration of H_2L is varied:

$$[(\text{Zr})_m(\text{H}_2\text{L})_n] = \frac{C_{\text{H}_2\text{L}}}{n}$$

If (A) is plotted versus CH_2L , a straight line is obtained with a slope_{II} = $\epsilon l/n$. The ratio of n to m is obtained by taking the ratio of the two slopes:

$$\frac{\text{Slope}_I}{\text{Slope}_{II}} = \frac{n}{m}$$

This method is used to trace the complex formation in dilute solutions by taking two sets of experiment. The absorbance was measured at 520 nm. Figure (5), indicates that the stoichiometry is 1:1.

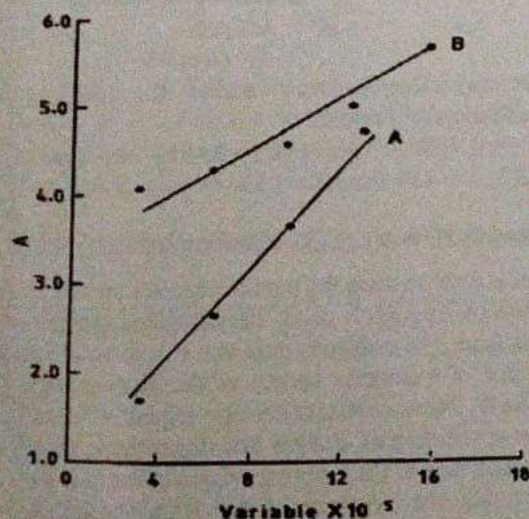


Figure (5): Slope ratio method.
 A = $[\text{Zr}^{\text{IV}}] = 7.8 \times 10^{-4} \text{ M}$; $[\text{ARS}] = 3.2 \times 10^{-5} - 1.92 \times 10^{-4} \text{ M}$.
 B = $[\text{ARS}] = 8 \times 10^{-4} \text{ M}$; $[\text{Zr}^{\text{IV}}] = 3.12 \times 10^{-5} \text{ M}$; $\lambda = 520 \text{ nm}$.

e) Limiting logarithmic method^(14,15):

This method proceeds in a similar fashion to that described in the slope ratio method, where the following equation is applied:

$$\log [(\text{Zr})_m(\text{H}_2\text{L})_n] \leftrightarrow m \log [\text{Zr}^{\text{IV}}] + n \log [\text{H}_2\text{L}] - \log K$$

On plotting the logarithm of the absorbance, which is proportional to the concentration of the coloured complex, against the logarithm of Zr^{IV} concentration, a straight line is obtained. Alternatively the slope of the straight lines gives the value of (m) and (n). In the first set of experiment, the concentration of Zr^{IV} was kept constant at $7.8 \times 10^{-4} \text{ M}$, with variable concentration of ARS ($3.2 \times 10^{-5} - 1.92 \times 10^{-4} \text{ M}$). The second set of the experiment is constructed, where the concentration of ARS was kept constant at $8 \times 10^{-4} \text{ M}$, while that of Zr^{IV} varied between ($3.12 \times 10^{-5} - 1.87 \times 10^{-4} \text{ M}$), Figure (6). The ratio n/m appeared 1, to allow that 1:1 species exists. Such conclusion goes in harmony with the above method. The absorption spectra of Zr-ARS complex for synthetic seawater samples showed two maxims at 418 and 512 nm. The former is due to the free ARS and the latter to Zr-ARS lake⁽⁶⁾. With the addition of fluoride the absorption at 418 nm increased due to the displacement and liberation of ARS from the lake by the fluoride. While at 520 nm the absorption decreased due to the destruction of the lake by the reaction of fluoride. With sufficient fluoride the maximum at 512 nm disappeared⁽⁶⁾. In the present work, the absorption spectra of Zr-ARS using ARS as a blank appears only at 520 nm. The addition of variable concentrations of fluoride ion ($0.5 - 3 \times 10^{-6} \text{ M}$), lead to decrease the intensity of the electronic absorption maxima at 520 nm.

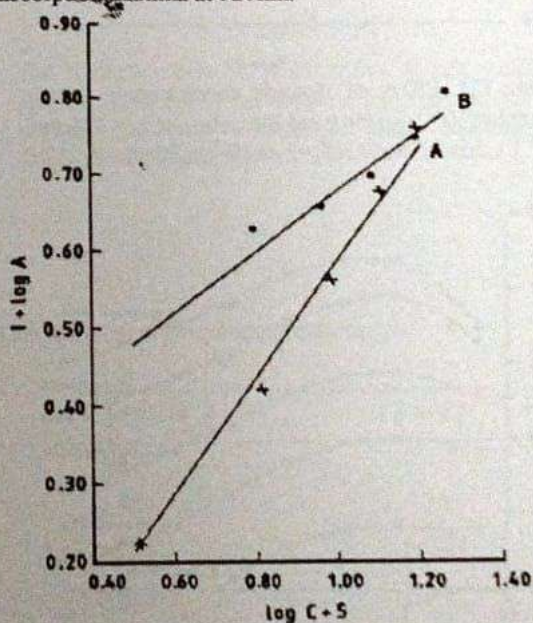


Figure (6): Limiting Logarithmic method.
 A = $[\text{Zr}^{\text{IV}}] = 7.8 \times 10^{-4} \text{ M}$; $[\text{ARS}] = 3.2 \times 10^{-5} - 1.92 \times 10^{-4} \text{ M}$.
 B = $[\text{ARS}] = 8 \times 10^{-4} \text{ M}$; $[\text{Zr}^{\text{IV}}] = 3.12 \times 10^{-5} - 1.87 \times 10^{-4} \text{ M}$;
 $\lambda = 520 \text{ nm}$.

2) Factors affect the Zr-ARS reaction:

i) Effect of acidity:

The effect of the addition of 0.42 N H_2SO_4 on both Zr-ARS and Zr-ARS-F complexes at 25°C and 30°C gave that, the H_2SO_4 media decreases the absorbance of the reddish violet complexes to be yellow in colour due to the formation of zirconium sulphato complex, $[ZrO(SO_4)_2]^{2-}$.

ii) Effect of blank:

The effect of the constituents of the blank on the electronic absorption spectra of Zr-ARS and Zr-ARS-F systems is studied. Different experiments were constructed for such purpose. In general, the intensity using distilled water as a blank is somehow higher than using ARS as a blank at 420 or 520 nm. The increase of the concentration of Zr^{IV} and ARS leads to increase the effective concentration of the complex with the increase of the corresponding absorbance. A remarkable feature is recorded when using Zr-ARS complex as a blank with a satisfactory wavelength for measuring at 420 nm, Figures (7,8).

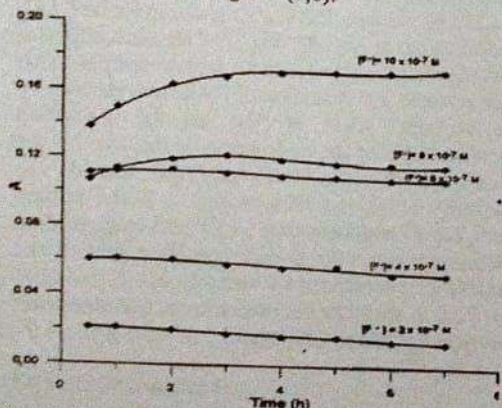


Figure (7): Effect of fluoride concentration on the spectra of Zr^{IV} -alizarin red S reaction at $\lambda = 420$ nm. $[Zr^{IV}] = 1.56 \times 10^{-4} M$; $[ARS] = 2.4 \times 10^{-4} M$, Blank = Zr-ARS

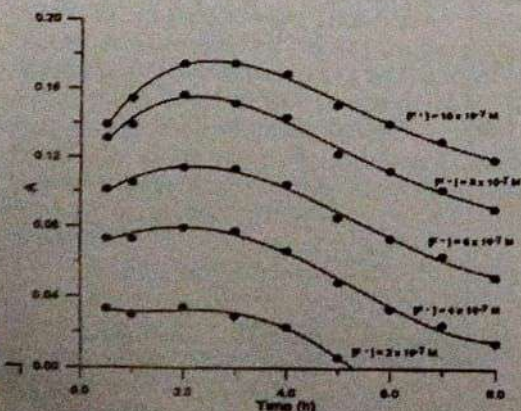


Figure (8): Effect of fluoride concentration on the spectra of Zr^{IV} -alizarin red S reaction at $\lambda = 420$ nm. $[Zr^{IV}] = 3.12 \times 10^{-4} M$; $[ARS] = 4.8 \times 10^{-4} M$, Blank, Zr-ARS

iii) The behavior in the synthetic seawater:

The absorbance for the reaction of $2.4 \times 10^{-4} M$ ARS with $1.56 \times 10^{-4} M$ $ZrCl_4$ in synthetic seawater is increased by the addition of solutions composed of different concentrations of F^- using Zr-ARS complex as a blank at 420 nm. The non-linearity is probably due to the especially interference of the divalent ions exist in synthetic seawater with Zr-ARS complex.

3) Validity of Beer's Law:

Spectrophotometric micro-determination of fluoride is applied using Zr-ARS reagent. The experiment is designed where the concentration of ARS was $2.4 \times 10^{-4} M$ while that of Zr^{IV} was $1.468 \times 10^{-4} M$, and variable concentrations of fluoride at $pH = 1.5$ and $\lambda = 420$ nm. The plot of (A) versus the variable concentrations of fluoride gives a straight line, Figure (9), up to $0.8 \times 10^{-6} M$. Beer's Law is obeyed under these conditions and can be used to determine the concentration of the unknown samples with fair accuracy.

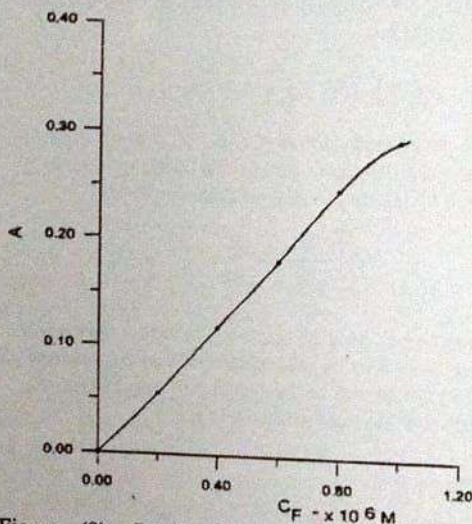


Figure (9): Beer's Law validity for different concentrations of fluoride.

$[Zr^{IV}] = 1.468 \times 10^{-4} M$, $[ARS] = 2.4 \times 10^{-4} M$, Blank: Zr-ARS, $\lambda = 420$ nm; $pH = 1.15$

4) The stoichiometry of Zr-ARS-F complex:

A trail is done to trace the possible species present in solution of Zr-ARS-F using the discussed straight-line method. The deduced value of $n = 1$, to point the formation of a complex species of the stoichiometry $Zr(ARS)F$. More confirmations are explained based on the application of straight line (logarithmic plot). The conclusion of the latter experiment gives also $n = 1$ to typify the existence of the 1:1:1 species. K (dissociation constant) was calculated and was found to be 8.79×10^{-4} , $pK = 3.056$, [where, $n = 0.556 \pm 1$, $\epsilon = 10000$, $a_0 = 0.0079 M$, $v_0 = 10$ ml, $V = 50$ ml and $b_0 = 0.01$ g/l F^- (1 ml of fluoride solution contains 10 $\mu g F^-$)].

5) Kinetics of the formation of Zr-ARS complex:

The kinetic investigations for the reaction of Zr^{IV} (4.8×10^{-4} M) with ARS (4.8×10^{-4} M) to form Zr-ARS complex were studied at different temperatures and fluoride ion concentrations in aqueous media. These investigations involve the effect of either temperature or fluoride ion concentrations on the reaction rate of Zr-ARS complex.

The change in absorbance at $\lambda = 520$ nm with time is taken as a measure for the concentration of Zr-ARS complex. The reaction was found to follow

the second order rate law. The specific rate constants were calculated from the following second order kinetic law⁽¹⁶⁾:

$$kt = \frac{1}{a-x} - \frac{1}{a}$$

(a) is the initial concentration of either reactants, (x) is the amount formed at time (t). From the slope of the linear plots of $1/(a-x)$ against the time, the second order rate constants were calculated, Table (1).

Table (1): The values of the rate constant at different temperatures for Zr-ARS reaction.

Temperature (°C)	20	25	30	35	40
$k \times 10^3 (\text{mol}^{-1} \text{l h}^{-1})$	1.892	1.939	2.293	2.598	3.359

Different concentrations of fluoride ion were added to equimolar quantities of Zr^{IV} and ARS, and the reaction was followed spectrophotometrically at

30°C. The reaction followed the second order rate law, Table (2).

Table (2): The rate constants of Zr-ARS reaction in presence of different concentrations of fluoride at 30°C.

$10^3 x [F]$	$-\log [F]$	$10 + \log [F]$	$k \times 10^3 (\text{mol}^{-1} \text{l h}^{-1})$	$3 + \log k$
0.8	7.096	2.904	3.12	0.949
1.6	6.795	3.205	3.57	0.552
2.0	6.698	3.302	3.53	0.548
4.0	6.397	3.603	5.24	0.719
6.0	6.221	3.779	6.68	0.825

6) Effect of temperature on Zr-ARS reaction rate:

The familiar Arrhenius relationship was applied⁽¹⁶⁾:

$$k = Ae^{-E_a/RT}$$

Where k is the rate constant, A is the frequency and T is the absolute temperature. An additional relationship is used to obtain ΔH^* from the experimentally derived E_a values:

$$E_a = \Delta H^* + RT$$

The Arrhenius plot of the logarithm of rate constant against reciprocal of the absolute temperature, gave a straight line with a negative slope amounts to $-E_a/2.303 R$, Table (3).

Table (3): The logarithm values of the rate constant of Zr-ARS reaction at different temperatures.

Temperature (°C)	$1/T \times 10^3 (\text{K}^{-1})$	$k \times 10^3 (\text{mol}^{-1} \text{l h}^{-1})$	$3 + \log k$
20	3.412	1.892	0.277
25	3.355	1.939	0.288
30	3.300	2.293	0.360
35	3.247	2.598	0.415
40	3.194	3.359	0.526

The activation energy of the reaction was calculated and was found to be $5.2692 \text{ K Cal mol}^{-1}$

and the enthalpy of activation for the reaction was calculated and collected in Table (4).

Table (4): Values of the enthalpy (ΔH) for Zr-ARS reaction at different temperatures.

Temperature ($^{\circ}\text{C}$)	20	25	30	35	40
ΔH (K.Cal.mol $^{-1}$)	4.6833	4.6733	4.6633	4.6533	4.6433

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