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College of SCIENCE, AL-MUSTANSIRIYAH
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CONTENT

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6. The same facts should not be given in tables and figures except when it is absoutely necessary to do so.
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8. Where possible, Papers should follow the Pattern: Introduction, Experimental, Results and Discussion.

Al-MUSTANSIRIYAH
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CONTENT

γ-RADIOLYSIS OF ACETOPHENONE P-CHLOROACETOPHENONE, p-NITROACETOPHENONE, MIXTURE OF ACETOPHENONE AND BENZOPHENONE, AND FLUORENONE IN BASIC ORGANIC AND AQUEOUS GLASSES AT 77 K.

Saad K. Ismail* and G. Scholes

ABSTRACT

The transient species formed during the γ-radiolysis of acetophenone and a mixture of acetophenone and benzophenone in basic aqueous and organic glasses at 77° K were studied spectroscopically and found to be absorbed at 430-445 nm. Another absorption is found to be located at 380 nm (in basic organic glass) which is assigned to the O^- adduct to acetophenone. Added acetone has no effect for the electron transfer to acetophenone while it is effective with benzophenone. The electron attachement is found to be due to the transfer between isopropanol radical anion and acetophenone in the case of p-chloro and p-nitro acetophenone the first is found to behave like acetophenone while the second has a different behaviour since it forms a quinone structure in basic medium giving a sharp absorption at 565 nm shifted to 550 nm which is unstable decayed to give two absorptions located at 490 nm and 525 nm. The 565 nm is attributed to the radical anion where the negative charge is delocalized. The mixture of acetophenone and benzophenone gives an indication of electron transfer between them. In the fluorenone

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system two weak absorption at 444 nm and 500 nm obtained and attributed to the fluorenone radical anion.

INTRODUCTION

From pulse radiolysis results of aquous and isopropanol solutions of acetophenone, Adams et al [1] and Beckett et al [2] respectively found an absorption located at 430-445 nm. In the presence of acetone and benzophenone (When radiolyzing acetophenone in isopropanol solution) [1, 3] Adams et al. have stated that in solution a simple three-stage electron transfer "Cascade" occur via,

$$\overset{\ominus}{\text{Acetone}} \qquad \overset{\ominus}{\text{Acetophenone}} \qquad \overset{\ominus}{\text{Benzophenone}}$$

In the γ-radiolysis of some organic glasses of fluorenone, Hirota and Weissmann [4] have noticed an absorptions at 445 nm and 500 nm at low temperatures. McClelland [5] noticed a narrow absorption at 450 nm with a shoulder overlapping it at 500 nm, and attributed both to the fluorenone radical anion. Hirota and Weissmann [4] have also studied the solvent, Cations present, and dilution effect on this radical anion. They found that using low concentration of the material, only a small contribution from the 450 nm absorption was obtained and vice versa.

EXPERIMENTAL

1) Materials:-

Potassium hydoxide is of B.D.H. Analar grade used without any further purification. Isopropanol (Hopkin and Williams) of spectrosol grade bottled under nitrogen gas was used without further purification. Methanol and acetone (Hopkin and Williams) are of Analar grade were used without any further purification. Acetophenone and p-chloro acetophenone were purified by two successive vacuum distillations in an atmosphere of dry nitrogen into a storage bulb attached to a vacuum line and only the middle fractions of the distillates were retained for use. Nitrous oxide (British oxygen Co.) was purified on a Vacuum line by several thaw -freeze-pump cycles.

Other materials used were purified either by recrystallization or fractionation. All aqueous solutions were prepared in triple distilled water.

2) Other experimental details are given in a previously published paper [6, 7].

RESULTS AND DISCUSSION

A) ACETOPHENONE SYSTEM:-

When acetophenone (3.5 mm) is γ-irradiated in 7M KOH glass at 77° K a broad and weak absorption at 430-445 nm was obtained after thermally annealing the samples Fig. (1).

This absorption is assigned to the acetophenone radical anion formed by direct elecgron attachment to the acetophenone molecule. The yield product is found to be very low which is attributed to the low solubility of the material in 7M KOH aqueous solution. This absorption is found to consist of two absorptions located at 330 nm and 344 nm and both were assigned to the acetophenone negative ion since they formed and decayed together. The electron attachment is illustrated below;

$$PhCOCH_3 + e^-_{tr} \xrightarrow{ann.} (CH_3COPh)^- \text{ .... } (1)$$

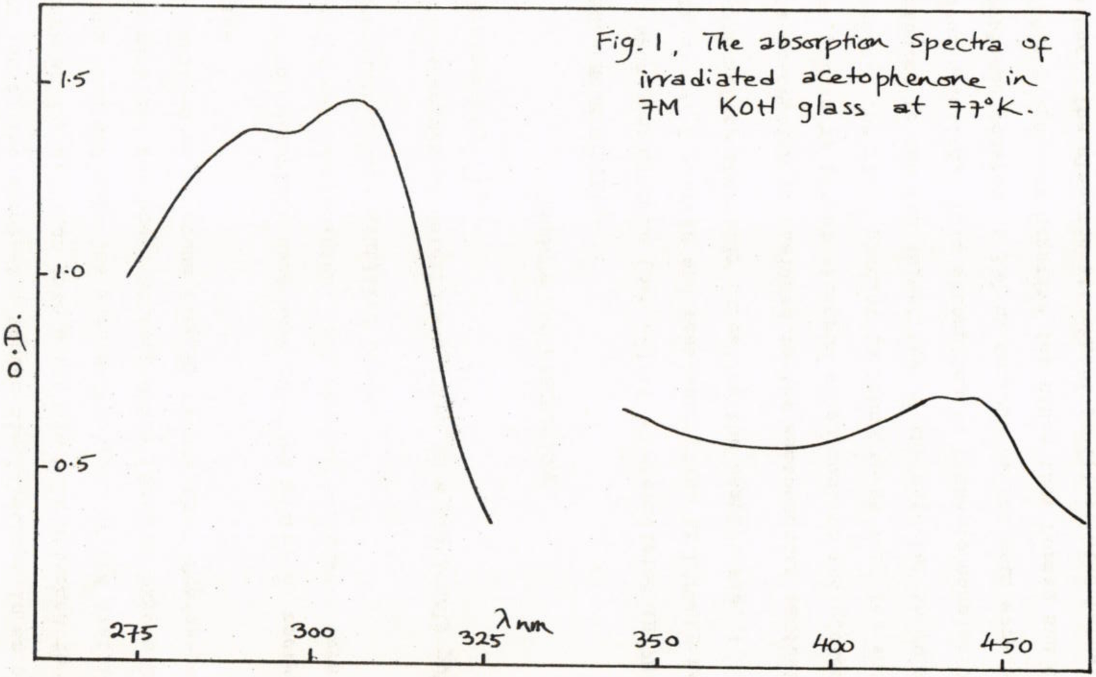
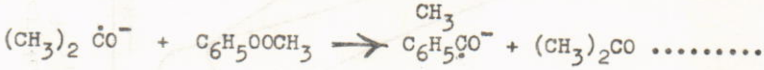


Fig. 1, The absorption Spectra of irradiated acetophenone in 7M KOH glass at 77°K.

Changing from glassy aqueous to basic isopropanol glassy medium (0.1M - 0.4M KOH) at 77° K, a greater yield at 440-450 nm Fig. (2) was obtained after irradiation which was increased in intensity after annealing the sample. However, after three successive annealings this absorption decayed to give a new weak absorption at 380 nm. The 440-450 nm absorption consists of two bands and are assigned to the acetophenone radical anion formed by anionic electron transfer from the isopropanol radical anion.

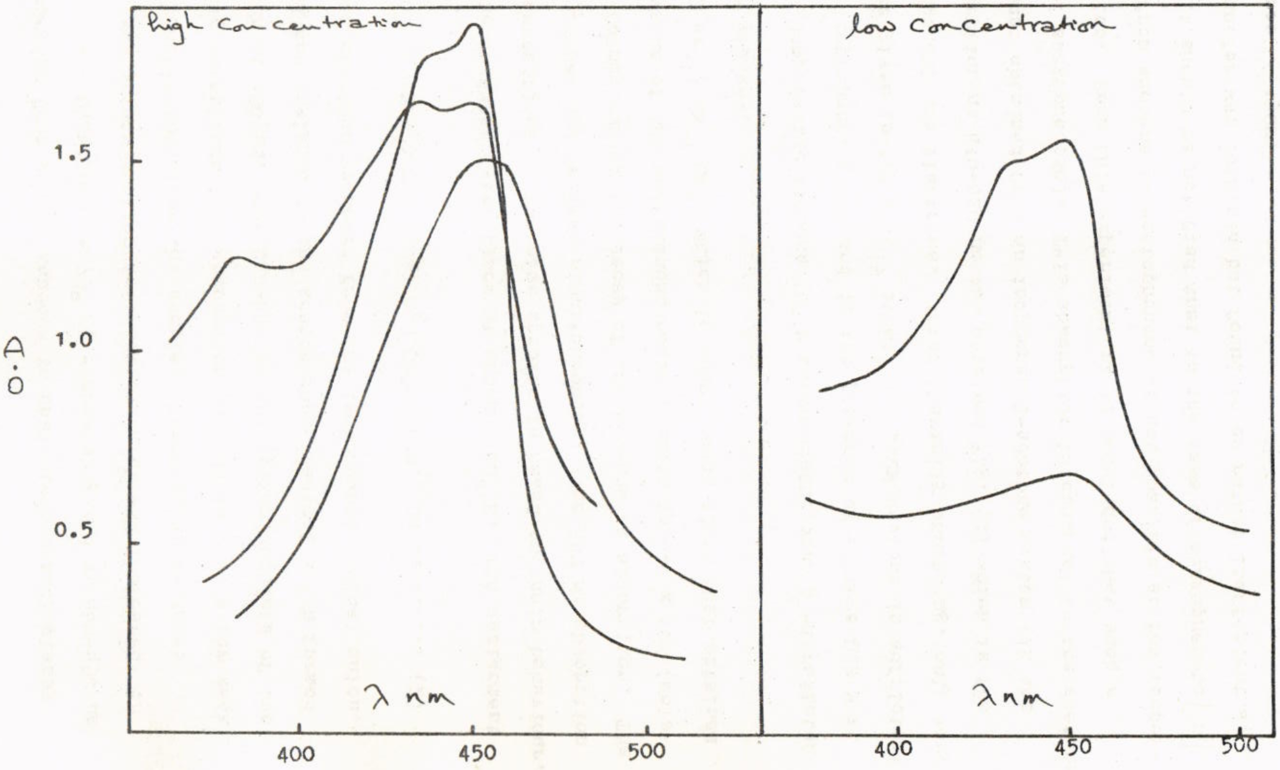


$$(CH_3)_2\,\dot{C}O^- + C_6H_5OOCH_3 \longrightarrow C_6H_5\overset{CH_3}{\underset{\cdot}{C}}O^- + (CH_3)_2CO \;\ldots\ldots\ldots \quad (2)$$

This transfer takes place at around 160° K. The assignment of both absorptions to the same species is based on their behaviour. They are formed and decayed simultaneously. The 380 nm absorption which is formed during the decay of the 440-450 nm absorption. The GE(450) value of the acetphenone radical anion is 9.2×10^3 (molecules 100 ev^{-1}) xM^{-1} Cm^{-1} which is about seven times that obtained in 7M KOH glasses.

For Comparative reasons 10^{-1}M acetophenone was γ-irradiated in basic isopropanol glass and in the presence of acetone 0.2 M at 77 K (Dose given is 3.3×10^{19} ev ml^{-1}). 0.2M acetone is sufficient to scavenge all the electrons. After thermally annealing, only very weak absorption at 410-420 nm was obtained Fig. (3) which is the same as that obtained from an isopropanol-acetone system (in the absence of acetophenone). This absorption is assigned to the acetone negative ion. From this experiment it is concluded that such a transfer from acetone to acetophenone is not possible at low temperatures. It should be notified that in the case of benzophenone [8] such a transfer was obtained but found to be rather inefficient at temperatures $<$ 150K.

Fig. 2, The absorption Spectra of irradiated acetophenone in basic isopropanol glass at 77° K.



These results suggested the following Scheme for the three-stage electron transfer between the three Ketones invastigated;

$$\begin{tikzcd} \overset{\ominus}{\text{Acetone}} \arrow[r, "/" marking] \arrow[rr, bend left, "\text{Slow}"] & \overset{\ominus}{\text{Acetophenone}} \arrow[r] & \overset{\ominus}{\text{Benzophenone}} \end{tikzcd}$$

When acetophenone is γ-irradiated in neutral methanol water glass at 77° K, an absorption at 420-430 nm Fig. (4) is observed immediately after irradiation which decayed very rapidly on annealing and is attributed to the neutral form of the acetophenone radical anion. This absorption was not obtained in the absence of water. If there is a back reaction as;

$$\mathrm{ROH^+(\Phi\, COCH_3)^-} \xrightarrow[\text{reaction}]{\text{back}} \mathrm{\Phi\, COCH_3 + ROH} \quad \ldots\ldots\ldots \; (3)$$

no product is expected. However, in the presence of water, this back reaction could be avoided as shown below to get the neutralized form of the acetophenone radical anion,

$$\begin{tikzcd} \mathrm{ROH^+\,(\Phi\, \dot{C}OCH_3)^-} \arrow[r, "H_2O"] \arrow[d, "H_2O"] & \mathrm{\Phi\, \dot{C}OHCH_3} \\ \mathrm{RO\cdot + H_3O^+ + (\Phi\, \dot{C}OCH_3)^-} \arrow[r] & \mathrm{(\Phi\, \bar{C}OHCH_3)} \quad \ldots\ldots\ldots \; (4) \end{tikzcd}$$

which is the same as that obtained by Beckett et al [2] . The phenomena of anionic electron transfer is found to occur from non-aromatic molecule to a highly aromatic molecule (acetone to benzophenone).

2) p-CHLORO ACETOPHENONE AND p-NITRO ACETOPHENONE SYSTEMS:-

The behaviour of p-Chloroacetophenone is found to be the same as that of acetophenone after γ-irradiation in basic isopropanol. The presence of nitrous oxide was found to decrease the product at

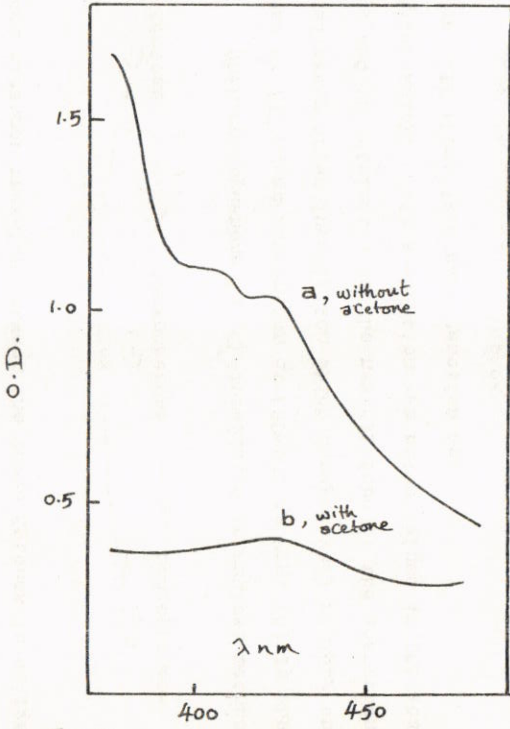


Fig. 3 The absorption spectra of irradiated acetophenone in basic Isopropanol glass at 77° K.

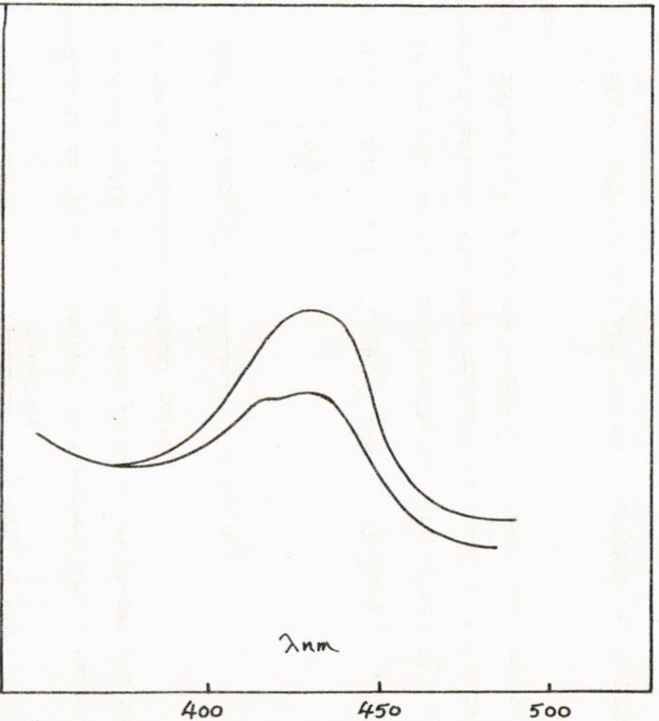
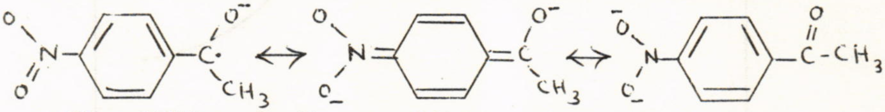


Fig. 4 The absorption Spectra of Irradiated acetophenone in methanol-water neutral glass at 77°K.

450-470 nm Fig. (5) which may be due to reaction between nitrous oxide and isopropanol radical anions (GE Calculated in the absence of nitrous oxide is 5.88×10^{-3} (molecules 100 ev)$^{-1}$ ($M^{-1} \times cm^{-1}$), and that in the presence of nitrous oxide is 1.98×10^{3} (molecules 100 ev^{-1}) ($M^{-1}Cm^{-1}$).

p-nitro acetophenone is γ-irradiated in neutral isopropanol at 77°K because of the formation of the quinone structure in basic medium giving a dark red colour. A neutral isopropanol glass containing p-nitroacetophenone gave a sharp absorption at 565 nm after irradiation which is decreased in intensity and shifted to 550 nm. This 550 nm absorption is found to be unstable at temperatures $>$ 140°K and decayed to two weak absorptions located at 490 nm and 525 nm Fig. (6). The 565 nm absorption is attributed to a species which is thought to be a radical where the negative charge is delocalized. The other two absorptions obtained at higher temperatures are assigned to the neutralized form of the above new species. Using low concentration of the material an additional absorption at 360 nm was obtained which is assigned to the same species mentioned above since it decays with the decay of the 565 nm absorption, which is supported by experiments [3]. The following structures of the above species are suggested;



The addition of nitrous oxide has only a little effect on the product.

3) MIXTURES OF ACETOPHENONE AND BENZOPHENONE SYSTEMS

When a mixture of benzophenone ($10^{-3}$to 3×10^{-3} M) and acetophenone (10^{-2} to 3×10^{-2}) is γ-irradiated in basic isopropanol glass at 77°K, a weak absorption at 440-450 nm was obtained. This absorption increased in intensity after annealing, and is assigned to the acetophenone radical anion formed via anionic electron transfer from the isopropanol radical anion. This absorption is

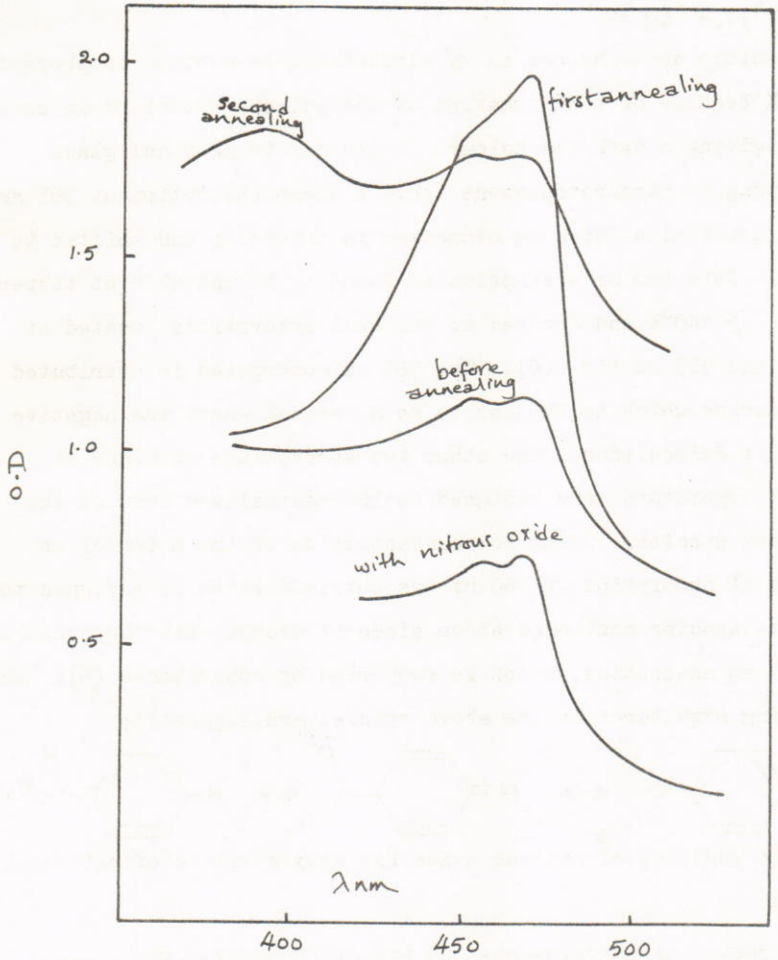


Fig. 5 The absorption spectra of p- Chloroacetophenone in basic isopropanol glass at 77°K.

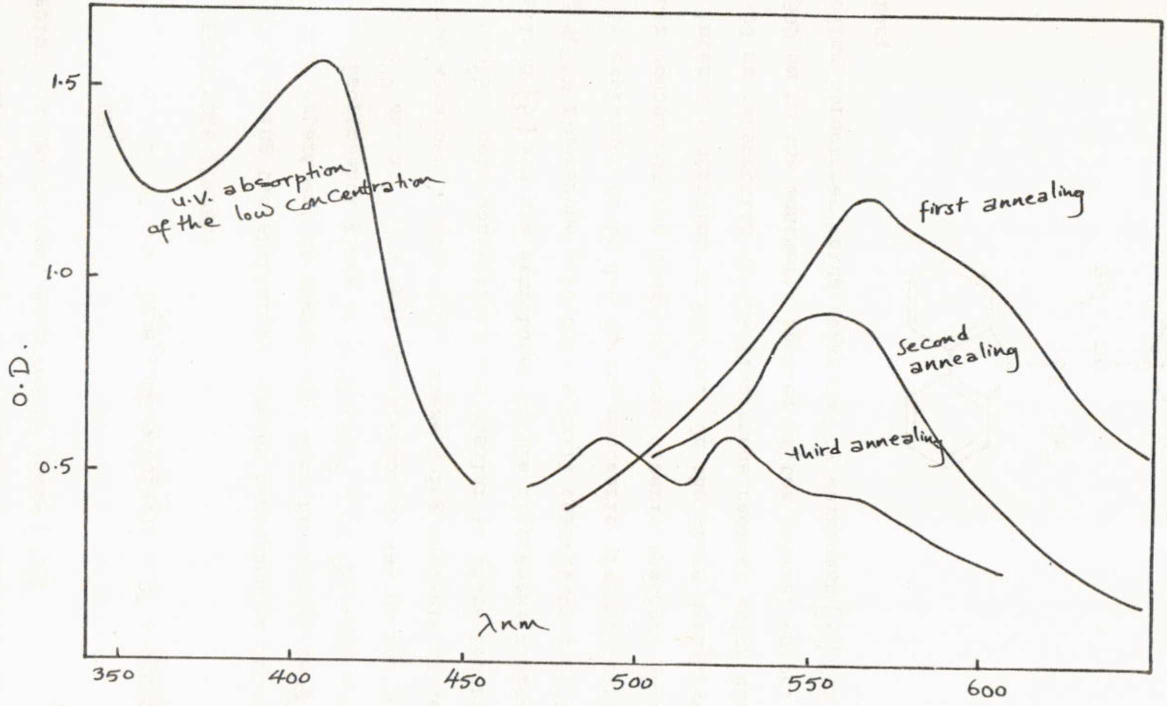
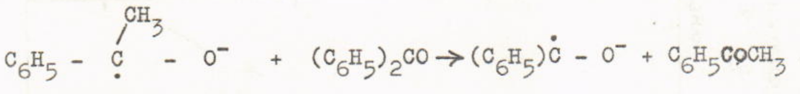


Fig.6 The absorption spectra of irradiated p-nitro acetophenone in neutral isopropanol glass at 77°K

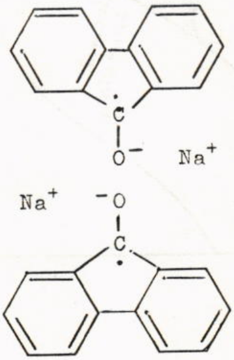
decreased in intensity after three successive annealings and a new absorption at 610 nm was produced. This later absorption is the benzophenone radical anion Fig. (7). It is concluded that there is a Charge transfer from acetophenone to benzophenone in such a medium similar to that reported by Adams [1,3];



$$C_6H_5 - \overset{CH_3}{\dot{C}} - O^- + (C_6H_5)_2CO \rightarrow (C_6H_5)\dot{C} - O^- + C_6H_5COCH_3 \quad \ldots(5)$$

4) FLUORENONE SYSTEM:

Considering the similarity between benzophenone and fluorenone, this experiment is suggested, When fluorenone is γ-irradiated in basic isopropanol glass at $77^{o}K$ (10^{-2} - $10^{-3}M$) with a dose of 3.31×10^{19} ev. ml^{-1} , a weak absorptions at 444 nm and 500 nm are obtained as shown in Fig. (8). These being unstable at temperatures above $160^{o}K$. Both absorptions are similar to those reported by McClelland [5] and are attributed to the fluorenone radical anion. Using $10^{-2}M$ fluorenone gave only a small contribution at 500 nm, this is explained to be due to the monomeric dimeric transformation (higher concentrations leads to more dimeric species) which gives a more intense absorption at 450 nm. On the above basis, we assigned the 450 nm absorption to the fluorenone radical anion dimer and the 500 nm to the monomeric species of the radical anion. The following structures being suggested by Weissmann [4] for thedimeric species;



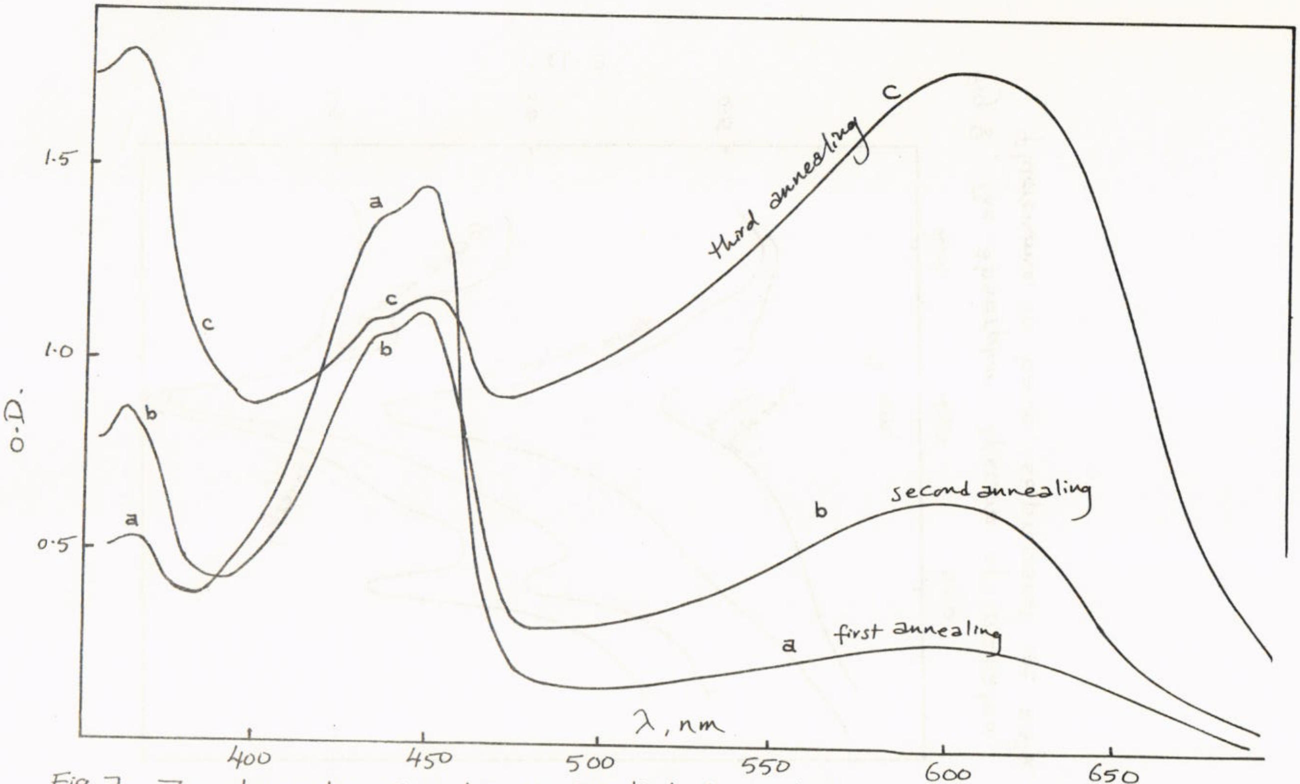


Fig.7. The absorption spectra of irradiated acetophenone and benzophenone basic isopropanol at 77°K.

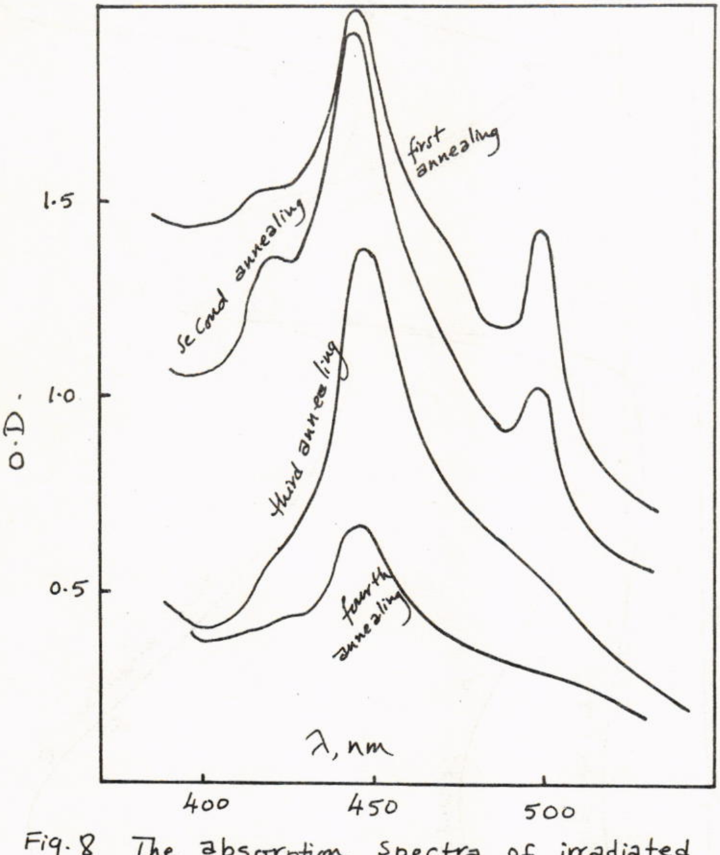


Fig. 8, The absorption spectra of irradiated fluorenone in basic isopropanol at 77°K.

REFERENCES

1) G.E. Adams B.D. Michael and J.T. Richards, Nature Vol. 215, No. 5107, 1248-50 (1967).

2) A. Beckett, A.D. Osborne and G. Porter, Trans. Farad., Soc., 60,873-881 (1964).

3) G.E. Adams, B.D. Michael and R.L. Willson, Advances in chemistry series No. 81 Radiation Chemistry I 289-307 (1968).

4) N. Hirota and S.I. Weissmann, J. Am. Chem. Soc., 86, 2538 (1964).

5) B.J. McClelland, Trans. Farad. Soc., 60, 1458-1471 (1961).

6) S.K. Ismail, Al-Mustansiriyah Journal of Science, Vol. 3 (1978).

7) S.K. Ismail, Al-Mustansiriyah Journal of Science, Vol. 2 (1977).

8) S.K. Ismail and G. Scholes, Al-Mustansiriyah Journal of Science, Vol. 4 No. 1 (1979).

-IRRADIATION OF POTASSIUM BROMIDE AND POTASSIUM THIOCYANATE IN 7M KOH GLASSES AT 77°K

Saad K. Ismail* and G. Scholes

ABSTRACT

The formation of Br_2^- in 7M KOH glass at 77° K was studied spectroscopically in the presence and the absence of N_2O. It has been found that the presence of nitrous oxide increases the yield product. The absorption at 360 nm is assigned to the Br_2^- radical anion. A competition between Br^- and ethanol towards O^- was also studied and it was found that the presence of ethanol decreases the absorption at 360 nm.

In the γ-irradiation of Potassium thiocynate in the same above glass (7M KOH at 77°K) gives three absorptions located at ; 370-380 nm, 420 nm and 475 nm. The first absorption is assigned to the O^- adduct ($CNSOH^-$) while the second absorption is probably due to $(SCN^-)_3$ ion and finally the last one is attributed to the $(CNS^-)_2$ radicsl anion. It has been found that the Presence of nitrous oxide increases the yield of $(CNS^-)_2$ radical anion.

INTRODUCTION

The formation of Br_2^- radical anion was studied by many authors in aqueous and organic media [1-4] . From flash Photolysis studies or mercury II halide complexes and ions in solution [5], the decay kinetics of the transient species formed in both netural and acid

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solution with the rates of reaction of Br_2^- with added solutes were reported. An absorption spectrum at 360 nm was obtained similar to those reported in flash photolysis [6, 7] and pulse radiolysis [8] . Other suthors [9] have reported the formation of Br_2^- at 360 nm in the pulse radiolysis of deareated alcoholic solutions of alkali **halides** In the pulse radiolysis of frozen aqueous HBr solution at 77°K Borisova and Bugaenko [10] reported the absorption of Br_2^- transient at 365 nm.

Buxton et **al.** [11], in the Pulse radiolysis of deareated solution of hydrohromite observed an absorption located of 360 nm and attributed it to Br_2^-. They also found that the addition of 0.1M NaOH decreases the yield which was attributed to the decrease in the primary oxidizing radical ($\bar{O}$).

It was been reported [12, 13] that on pulsing solutions of thiocyanate ions in the presence of air or **nitrous** oxide, to eliminate the e_{aq}^- absorption, a strong transient absorption at 475 nm is produced. This results from the reaction of OH radicals, indicated by the fact that in the nitrous oxide system, the absorption is increased by the amount expected due to the production of more OH **radicals** It was Postulated by Baxendale et al. [14] that the thiocyanate behaved as a pseudohalide forming $(CN\bar{S})_2$,

$$CNS + CN\bar{S} \overset{K}{\rightleftharpoons} (CN\bar{S})_2 \text{ .... } (1)$$

and that the absorption band at 475 nm was due to $(CN\bar{S})_2$. The equilibrium constant for the above reaction was calculated as $1.2 \times 10^5 M^{-1} Sec^{-1}$. Dainton et al. [15] assigned the absorption at 470 nm obtained from the pulse radiolysis of CNS^- ions in methanol to the formation of $(CNS^-)_2$.

EXPERIMENTAL

1) Materials:- Potassium bromide, Potassium thiocyanate and potassium hydroxide are of Analar grade from B.D.H. and they were used with out any further purifications. Nitrous oxide from the British oxygen company was purified by distillation several times on a vacuum line and then stored in a pyrex vessel at liquid nitrogen temperature. Ethanol was used with out any purification since it is of sepectrosol grade (Hopkin and Williams) bottled under nitrogen gas. All aqueous solutions were prepared using triple distilled water.

2) The experimental details of thermal annealing and resolution of the absorption bands are given in a previous paper [16].

Irradiation and dosimetry, optical absorption measurements at 77 K, Variable temperature unit, sample preparation and photobleaching processes are all given in a previous paper [17] .

RESULTS AND DISCUSSION

A) Potassium Bromide system:-

γ-irradiation of high Concentrations ($>$ 0.2M) of potassium bromide in 7M KOH glass at 77°K give an intense absorption mainly located at 360 nm as shown in Fig. (1). An increase in the intensity with a slight shift of the above absorption band was obtained on thermally annealing the sample. A similar yield was obtained using lower concentrations of KBr and by the addition of nitrous oxide. It is reasonable to assign the above absorption to Br_2^- which may be formed according to the following reactions:

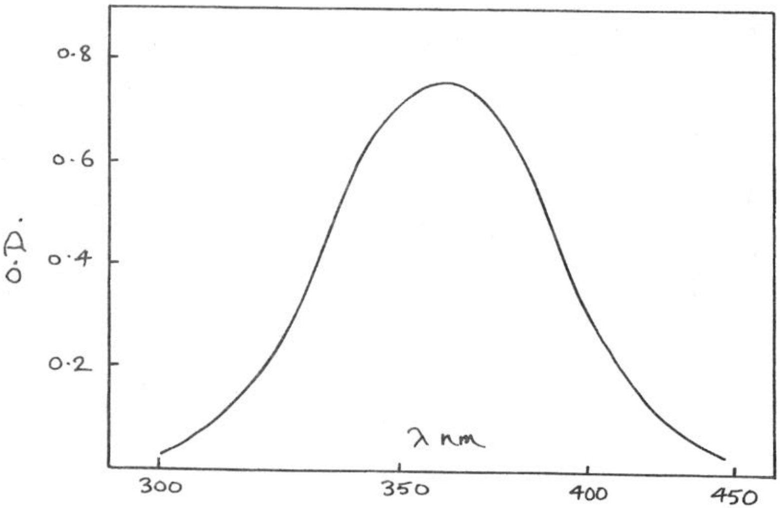

Fig. 1 The absorption spectrum of Br_2^- radical anion from the irradiated Br^- in 7M KOH glass.

$$Br^- + OH \dashrightarrow BrOH^- \qquad \text{.........} (2)$$

then either

$$BrOH^- + Br^- \dashrightarrow Br_2^- + OH^- \qquad \text{.........} (3)$$

or

$$Br^- + O^- \dashrightarrow BrO^{2-} \qquad \text{.........} (4)$$

$$BrO^{2-}\ Br^- \dashrightarrow Br_2^- + O^{2-} \qquad \text{.........} (5)$$

While in the presence of nitrous oxide, we have;

$$N_2O + e^- \dashrightarrow N_2O^- \rightarrow N_2 + O^- \qquad \text{.........} (6)$$

then either N_2O^- or possibly formed O^- react with Br^-;

$$N_2O^- + Br^- \dashrightarrow N_2OBr^{2-} \qquad \text{.........} (7)$$

then;

$$N_2OBr^{2-} + Br^- \dashrightarrow Br_2^- + \qquad \text{.........} (8)$$

All the above mentioned reactions are assumed to occur at higher temperatures. No intermediate was obtained on band analysis. These experiments do not rule out the precursor since it may absorb at the same wavelength as Br_2^-. The $G(Br_2^-)$ evaluated from the above experiments is found to be 0.49 ± 0.04.

Fig. (2) shows the absorption bands obtained from several experiments in which 0.2M KBr was γ-irradiated in 7M KOH glass at 77° K and to which a fixed amount (3 atmospheres) of nitrous oxide was added as well as different concentrations of ethanol (5×10^{-3} M-8×10^{-4}M). All the samples were photobleached and thermally annealed. A linear relation ship Fig. (3) was obtained by plotting the optical density at 360 nm after annealing versus ethanol concentration. A similar relationship was obtained by

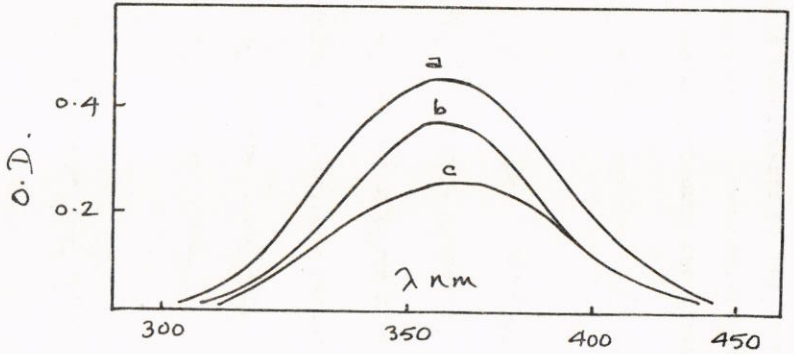

Fig. 2 The absorption spectra of Br_2^- radical anion in the Competition study with ethanol, a) 8×10^{4} M ethanol, b) 10^{-3} M ethanol, c) 5×10^{-3} M ethanol.

plotting 1/O.D. versus ethanol concentration. The decrease in the above absorption is attributed to a competition between Br^- and ethanol towards O^-. From the slope of Fig. (3) and the following relations:

either $Br^- + O^- \dashrightarrow$ product .... (9)

or O^- + ethanol $\dashrightarrow$ product .... (10)

It is evaluated $K_{10}/K_9 = 71.7$, which proves that Br^- is much weaker than that I^- towards O^-.

B) POTASSIUM THIOCYANATE SYSTEM:-

When 0.2M potassium thiocyanate in 7M KOH glass at 77°K is γ-irradiated with a dose of 2M rads and then annealed after photobleaching the trapped electrons, a successive absorption bands were obtained located at 370-470 nm Fig. (4).

The above absorption bands were obtained by thermally annealing the sample up to 160° K. Analysis of these bands gave three absorptions located at 370-380 nm, 420 nm and 475 nm as shown in Fig's (5, 6, 7). Since the medium is 7M KOH most of the holes will be in the form of O^-. The following reactions may occur.

$CNS^- + O^- \dashrightarrow (CNS\ O)^{2-} \overset{H_2O}{\rightleftharpoons} CNS + O^{2-}$ .... (11)

then the intermediate $(CNSO)^{2-}$ or CNS radical react with another CNS^- ion to form $(CNS)_2^-$ radical anion:

$(CNSO)^{2-} + CNS^- \dashrightarrow (CNS)_2^- + O^{2-}$ .... (12)

or

$CNS + CNS^- \dashrightarrow (CNS)_2^-$ .... (1)

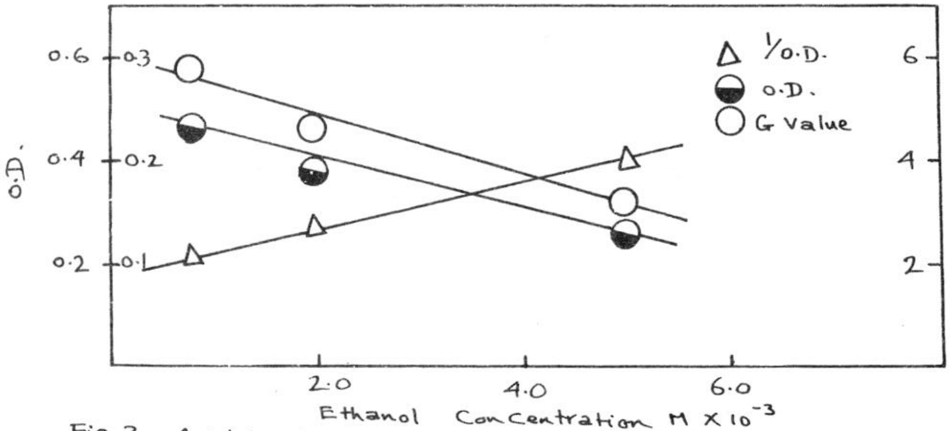

Fig. 3 A plot of O.D., 1/O.D. and $G(Br_2^-)$ versus ethanol concentration.

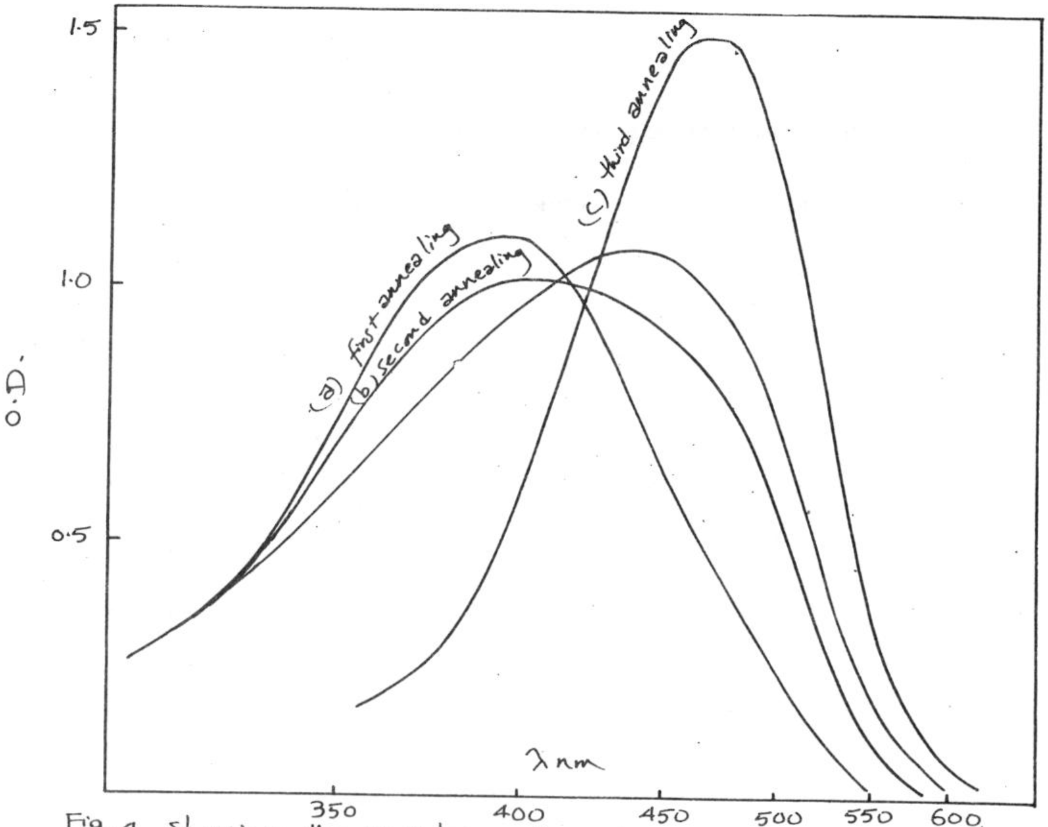

Fig. 4 showing the envelope absorption spectra of 0.01M KCNS irradiated in 7M KOH glass at 77°K.

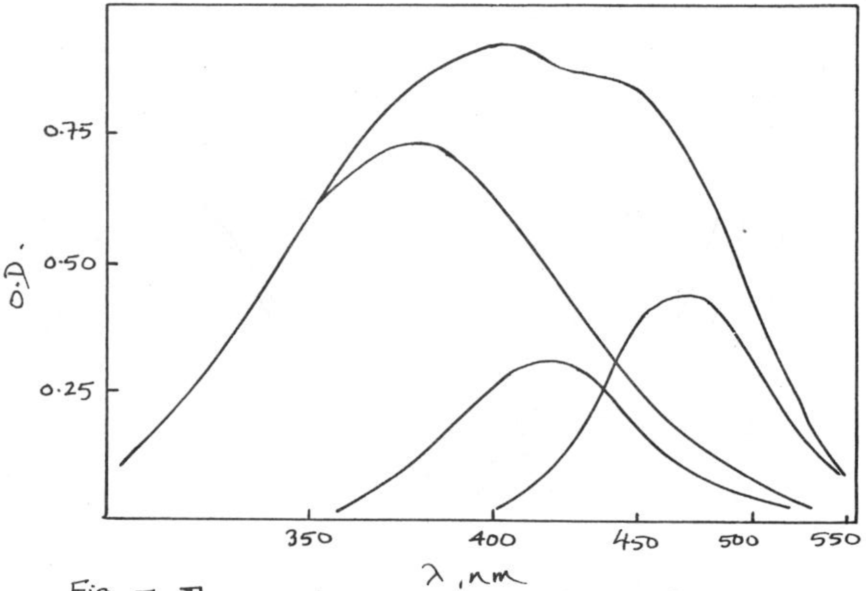

Fig. 5, The resolved absorption bands from (4b).

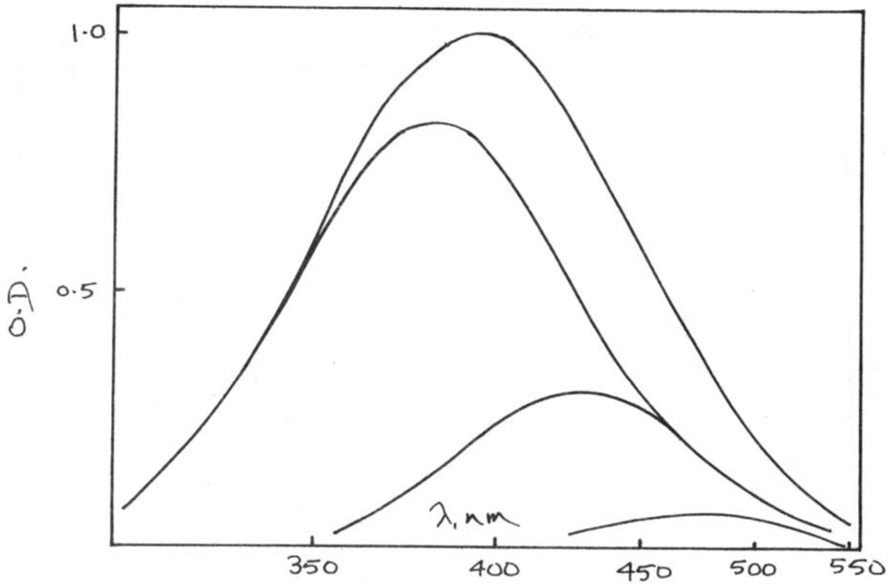

Fig. 6 The resolved absorption bands from (42).

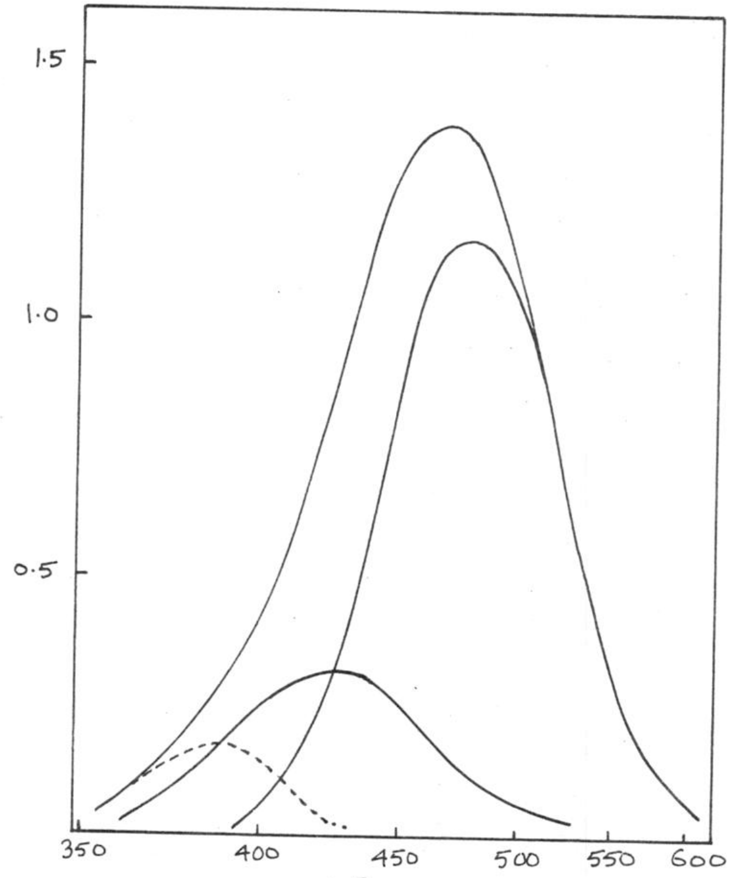

Fig.7 The resolved absorption bands from (4C).

Pulse radiolysis experiments of aqueous thiocyanate solution indicated that the PK of $CNSOH^-$ is > 14. Although in these highly alkaline glasses, the doubly charged form may exist, for the sole purpose of convenience, the hole adduct is written as $CNSOH^-$ and the following reactions are proposed:

$$CNS^- + OH \longrightarrow CNSOH^- \quad \ldots\ldots\ldots\ldots (13)$$

$$CNSOH^- + CNS^- \overset{H_2O}{\rightleftharpoons} (CNS)_2^- + OH^- \quad \ldots\ldots\ldots\ldots (14)$$

The absorption band at 475 nm is attributed to $(CNS)_2^-$ and that at 380 nm is assigned to the O^- adduct or $CNSOH^-$. These adducts are found to be unstable at higher temperatures. The absorption at 420 nm is probably due to $(CNS)_3^-$. It is formed in the first stage of the annealing processes and possibly via the reaction sequence:

$$2CNS \longrightarrow (CNS)_2 \quad \ldots\ldots\ldots\ldots (15)$$

$$(CNS)_2 + CNS^- \longrightarrow (CNS)^-_3 \quad \ldots\ldots\ldots\ldots (16)$$

The above 420 nm species was found to be stable at higher temperatures and to decay together with the decay of $(CNS)^-_2$ radical anion. From the above results the $G(CNS)_2^-$ is found to be 0.17. from some experiments carried out in the same laboratory, it has been found that the yield product of $(CNS)_2^-$ is linear with dose up to 0.2 Mrads. Considering the above linearity with dose and the dose given in the above experiment which is 2 Mrads a recalculation for $G(CNS)_2^-$ was carried out to give $G(CNS)_2^- = 1.68$.

It has been found out that the addition of (3 atmospheres) nitrous oxide to γ-irradiated 0.2M (KCNS) in 7M KOH glass at $77\ K^{o}$ increases the yield of $(CNS)_2^-$ and the ratio of (O.D. with N_2O)/(O.D. without N_2O) = 1.55 the above increase is attributed to the reaction between nitrous oxide and the **mobile** electron produced photochemically:

$$N_2O \quad + \quad e_m^- \quad \dashrightarrow \quad N_2O^- \qquad \ldots\ldots\ldots\ldots \ (17)$$

Then the above formed N_2O^- may act as an oxidizing agent to give more yield product:

$$(CNS^-) \quad + \quad N_2O^- \quad \dashrightarrow \quad (CNS \ . \ N_2O)^{2-} \ \ldots\ldots\ldots \ (18)$$

$$(CNS.N_2O)^{2-} + CNS^- \dashrightarrow (CNS)_2^- + .N_2O^{2-} \ \ldots\ldots\ldots \ (19)$$

Using lower thiocyanate concentrations (0.01 M) leads to a shift of the absorption at 380 nm to 370 nm which is explained to be due to the change in the glassy medium since the concentration has been changed to 1/20.

REFERENCES

1) M.S. Matheson, W.A. Mulac, and J. Rabani, J. Phys. Chem., 67,2613 (1963).

2) R. Devonshire and J. J. Weiss, J. Phys. Chem., 72, 3815 (1968).

3) F. S. Dainton and D. M. Brown, 5019, 195-6 (1966).

4) B. Cercek, M. Ebert, J. P. Keene and A. J. Swallow, Science, 145(3635 , 919 (1964).

5) M. E. Langmuir and E. Hayon, J. Phys. Chem., 71, 3808-14 (1967).

6) L. I. Grossweiner and M. S. Matheson , J. Phys. Chem. 61, 1089 (1957).

7) M. Anbar and J. K. Thomas. J. Phys. Chem., 68, 3829 (1964).

8) M. S. Matheson, W. A. Mulac, J. L. Weeks, and J. Rabani, J. Phys. Chem., 70, 2092 (1966).

9) S. Arai and A. Kira. J. Phys. Chem., 74,2102 (1970).

10) E. N. Borisova and L. T. Bugaenko, M. V. Lononosov, Moscow state University, Translated from Khimiya Vysokikh Energii, Vol. 3, No. 3. P.279 (1969).

11) G. V. Buxton, F. S. Dainton and F. Wilkinson, Chem. Commun., 11, 320-21 (1966).

12) G. E. Adams et al., Trans Farad. Soc., 61, 1674 (1965).

13) G. E. Adams, J. W. Boag, J. Currant and B. D. Michael "Pulse Radiolysis" Ed. M. Ebert et al., Academic press. (London) P. 117 (1975).

14) J. H. Baxendale, P.L.T. Bevan and D. A. Scott, Trans. Farad. Soc., 64, 2398 (1968).

15) F. S. Daniton, I. V. Janovsky and G. A. Salmon, Chem. Commun, 335 (1969).

16) S. K. Ismail and G. Scholes, Al-Mustansiriyah Journal of Science, Vol. 4, No. 1 (1979).

17) S. K. Ismail, Al-Mustansiriyah Journal of Science, Vol. 3 (1978).

CHEMICAL CONTROL OF RADIOPHARMACHUTICALS.

A. M. Al-Hilli and A. F. Roomaya*

ABSTRACT

The Chemical control of radiopharamaceuticals which includes radiochemical purity, chemical purity checks together with the sources of impurities and the methods used for their estimation were defined and explained. The methods used for determination of the main constituent of the product.

INTRODUCTION

The following radiopharmaceuticals are produced: Isotonic solution I-131, Rose Bengal labelled with I-131 solution, Hippuran labelled with I-131 solution, Triclein labelled with I-131 solution, Oleic acid labelled with I-131 solution, Human serum albumin labelled with I-131 solution, Colloidal Au-198 solution, Tc-99m heptavalent-in isotomic solution from Mo-99-Tc-99m, Generator., Neohydrin Hg-197 solution p-32 isotomic solution.

The radiopharmaceutical term means any inorganic compound containing the radioactive aspecies concerned, which are administered to human being for diagnostic and therapeutic applications, in vivo or as clinical diagnostic agent in vitro, usually they are dispehsed in aquous, hydro alcoholic and oily solutions or colloids.

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Al-Mustansiriyah Journal of Science, Vol. 4, No. 2 (1979).

As these radiopharmaceuticals administered to human beings they should be subjected to rigorous and stringent quality control. The quality control carried out on radiopharmaceuticals differ in some respects from those carried out on conventional pharmaceuticals and includes three main topics which are chemical, physical and biological investigations. We are concerned here with the chemical control of these preparations. Besides these preparations containing radioactive materials the contents of them are too minute therefore special and sensitive methods are used. The chemical control of these preparations takes different forms according to the requirements of the final product.

EXPERIMENTAL

1. Radiochemical purity:

Table (1) shows the common radiochemical impurities in radiophermaceuticals and methods used for their estimation. This term of purity is unique to radiopharmaceutical preparations and expressed as percentage of the radioactivity of the radionuclide in a certain chemical form to the total activity of the product, if a higher percentage of the radionuclide, than the permissible quantity is present in other chemical form than the stated or desired one, the product considered radiochemically impure, reasonable amounts of non-radioactive impurities can be tolerated while radiochemical impurities could not be so. Those radiochemical impurities may arise as a result of uncontrolled chemical reaction during processing of the target material or due to chemical instability of the compound in the product owing to radiolysis or radioassociation leading to displacement of

TABLE (1) The common radiochemical impurities in Radiopharmaceuticals and methods used for their estimation.

Radiopharmaceutical Prep.	Method	Support	Solvent or electrolyte	Time	Voltage in volts	Rf. or migration of molecules	Radio-chemical impurities	Rf. or migration of impurities
I-131	P.Ep.	W.No. 1	Phosphate buffer	40 min	400	11-11.5 cm.	IO_3^-	3-3.5 cm (7-75 Cm.)
Hippuran-I-131	P.Ep.	W.No. 1	Phosphate buffer	50 min	250	45-5 cm.	I^-	9.5-10 cm.
Rose Bengal-I-131	P.Ep.	W.No. 1	Phosphate buffer	50 min.	250	2-2.5 cm.	I^-	9.5-10 cm.
Human serum Albumin -I-131	P.Ep.	W.No. 1	Borate buffer	50 min.	250	5.5-6 cm	I^-	9.5-10 cm.
Colloidal-Au-198	Asc.ch.	Alhalinity Free W.No.1	Acetone 35 ml. water 10 ml adjusted to Ph 1.5-2 with conc. HCL	3 hr	-	0	Ionic Au	1.0
Sodium pertechnetate-Tc-99m	P.Ep.	W.No. 1	Phosphate buffer	80 min	400	8.5-9 cm	Low valency Tc.	< 5 Cm. 9.5-10 cm
Sodium Orthophosphate-P-32	Asc. ch.	W.No. 1	Trichoracetic acid solution solution 25 ml water 10 ml Acetone 65 ml	16-17 hr.	-	0.7-0.75	$P_2O_7^{4+}$	0.55 - 0.6

P.Ep.=Paper electrophoresis

Asc. ch = Ascending chromatography

W = Whatman chromatography grade paper.

the radionuclide within the molecular structure of the compound which occurs during shelf-life. Therefore radiochemical impurities must be kept to a minimum by taking in consideration the above mentioned causes, rather so they can give faulty diagnosis, later erroneous conclusions and act as a source of undesirable radiation to other organs in the body.

In order to safeguard the radiochemical purity of the preparations they should be made of optimum PH, moderate specific activity and stored in a cool dark place.

The methods used for the determining of radicchemical purity, are based on various physico-chemical techniques, which enable the different chemical forms of the radionuclides to be separated. Paper chromatography, paper electrophoresis, thin layer chromatography and ion-exchange are techniques in common use for this purpose.

2. Chemical purity:

Chemical purity of a radioactive preparation concerns the limits of other non-radioactive elements present in the final product.

The target material used for production of the radioisotopes and chemical reagents used in processing are of the highest grade of purity to overcome chemical impurities, besides that the chemical techniques involved in production of the radioisotopes are methods of purification like distillation, solvent extraction, precipitation and ion-exchange. Moreover chemical purity check should be done periodically on the products because these impurities may be the sort that would constitute a risk if administered medically such as the

the commonly known toxic elements like arsenic, mercury lead, antimony and tellurium. The last one is likely contaminant of I-131, which is prepared from irradiated Te O_2 targets. Or they may be entirely non-toxic but present in sufficient amount which interfere with the normal behaviour of the isotope.

Impurity limits could be detected by selection of a method used to determined small quantities of elements in the product. Emission Spectrography Table (2) is a convenient technique for the reason that many elements can be detected simultaneously using minute volumes of the active materials. The limitation of this technique is the contamination results from the vapours of the active material during sparking and the long time the process consumed compared with the rapid time of delivery of the product to the consumers. Therefore polarography is more suitable and could be used for the determination of most elements with less elaborate arrangements and manipulation without vapour contamination and takes much less time.

In the absence of these facilities one can adopt semiquantitive methods and spots test of heavy elements in the final product. But the disadvantage of this method is its sensitivity beyond the limits of most elements present in the final products.

3. Quantitative determination of main constituent in the final product:

One of the important factors that affects the existance of radioisotopes in the body are their biological halflives, which are different from one element to another. Nevertheless all radioisotopes considered to be toxic (with different

TABLE - 2 showing the lements commonly present in radiopharmaceuticals and the limits of their detection by Emission spectrography.

Element	Analytical line in A	sensitivity limit of the element Ug/ml	%error
Zn	2138	semiquantitatively	-
Cd	2265.02	1	± 18
As	2349.84	1	± 13
Te	2395.76	1	± 13
Cu	2492	0.1	± 18
Hg	2536.5	2.5	Easily subline by heat of the arc.
Sb	2598.06	1	± 10
Fe	2599.57	0.2	± 18
Be	2650.78	0.005	± 10
Mn	2801.09	0.01	± 10
Pb	2833.07	0.2	± 10
Cr	2835.63	0.2	± 10
Sn	2839.99	0.2	± 10
Ni	3050.7	0.2	± 10
Bi	3067.7	0.2	± 10

degrees of toxicity). Therefore is is preferable to give as much as possible a small amount of the radioactive material to the body using radioactive preparations of high specific activity.

From the above mentioned purpose and for estimating the specific activity of the product especially for those organic labelled preparations, the determination of the main constituent in product should be done. Various analytical methods have been adopted for the purpose: polarography, colorimetry, spectroghotometry and potentiometric titration are the most suitable techniques available. The selection of the method depend upon concentration and chemical character of the substance under consideration. The main constituent of most preparations produced generally are absorb in the ultraviolet and visible region of the spectrum in which spectrophotometric Table (3) and colorimetric methods can be applied, while the concentration of NaCl, KCl and NaBr in isotonic solutions of NaCl-24, KCl-42 and Na Br-82 can be determined potentiometrically.

A part from the main constituent in the product there were other determinations like buffer concentration as in the isotonic solutions of NaI-131 and P-32 and particle size as in collodial Au-198 solution which were estimated spectrophotometrically [1].

TABLE 3 Spectrophetometric determination of main constituent of radiopharmaceuticals produced

Radiopharmaceutical preparation	The determined const.	conc. of the const. in the prep.	Reagent if any and dilluent	λ max. mμ
Hippuran I-131	O-iodohippuric acid.	2-5 mg/ml	Water	235
Rose Bengal I-131	Total Halog. flucresceins	0.5-1.0 mg/ml	0.1 M Na_2HPO_4	550
Human serum Albumin-I-131	Human serum Albumine content	5-10 mg/ml	1% benzyl alcohol in water	280
Colloidal-Au-198	Gold content	4-5 mg/ml	Water	526
Sodium Iodide I-131	Phosphrous content	3.3-3.9 mg.ml.	Molyhdate Vanadate reagent + 30% HNO_3 and water.	410
Sodium Ortho-phosphate- P-32	**Phosphrous content**	3.3-3.9 mg/ml.	Molyhdate Vanadate reagent + 30% HNO_3 and water	410

DISCUSSION

It has been shown that the chemical control of radiopharmaceuticals is essential and important and in particular the radiochemical purity check which would be done regularly, and in time, on the products prior to their delivery to the consumers.

Our inferances about the chemical purity of the products is to be checked on the target materials prior to irradiation, in the mean time chemical purity determination could be done consequently from time to time on the products after delivery.

The benefit of all chemical controls is to give an idea for suitibility and reliability of the products for medical use.

Fig. (1) shows a histogram for radiochemical purity of isotonic solution of NaI-131, Fig. (2) histogram of radiochemical purity of Hippuran-I-131, Fig. (3) histogram of radiochemical purity of Triolein-I-131, Fig. (4) histogram of radiochemical purity of Tc-99m, Fig. (5) histogram of radiochemical purity of colloidal Au-198.

REFERENCES

1. R.A. Caro et al, "Int. J. of Appl. Rad. & Isotopes, Vol. 18, P. 327, (1967.)

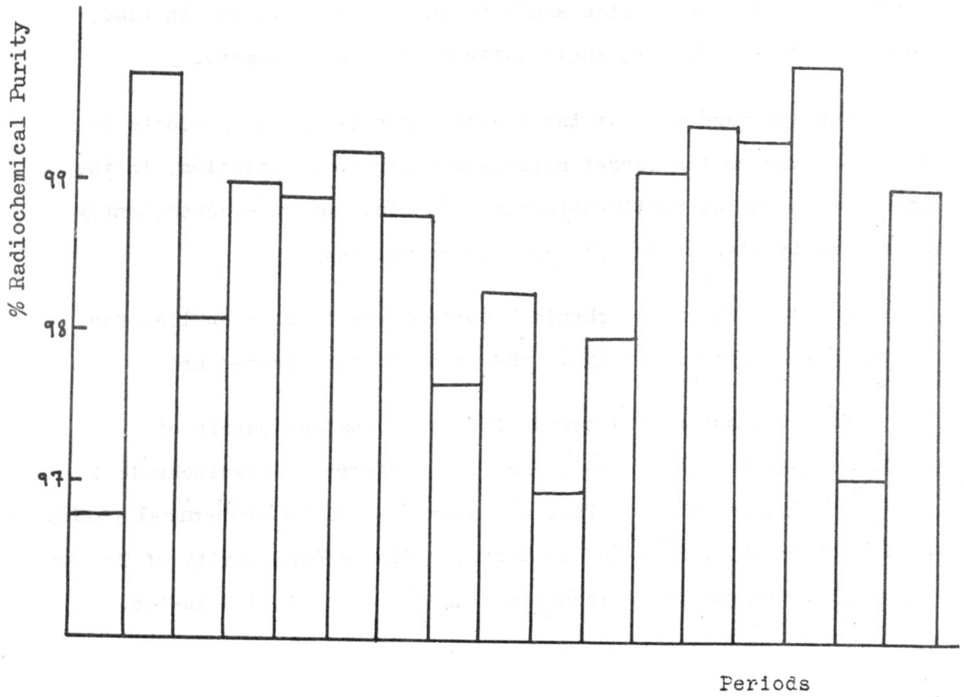

Fig. (1). A histogram showing radiochemical purity of isotonic solution of NaI-131 during 5 years.

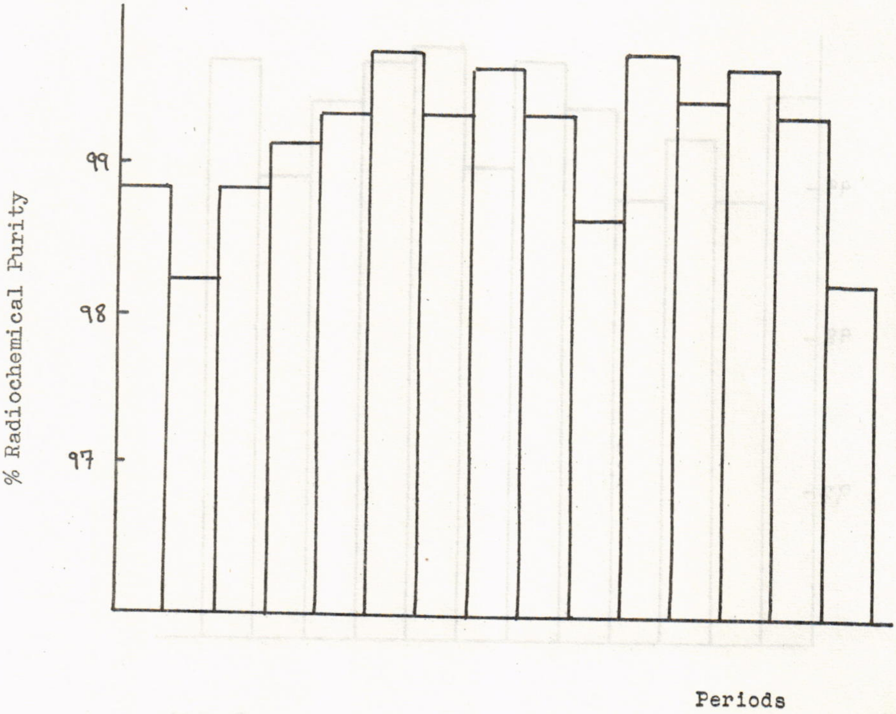

Fig.(2). A histogram showing radiochemical purity of different batches of Hippuran-I-131 solution during 4 years.

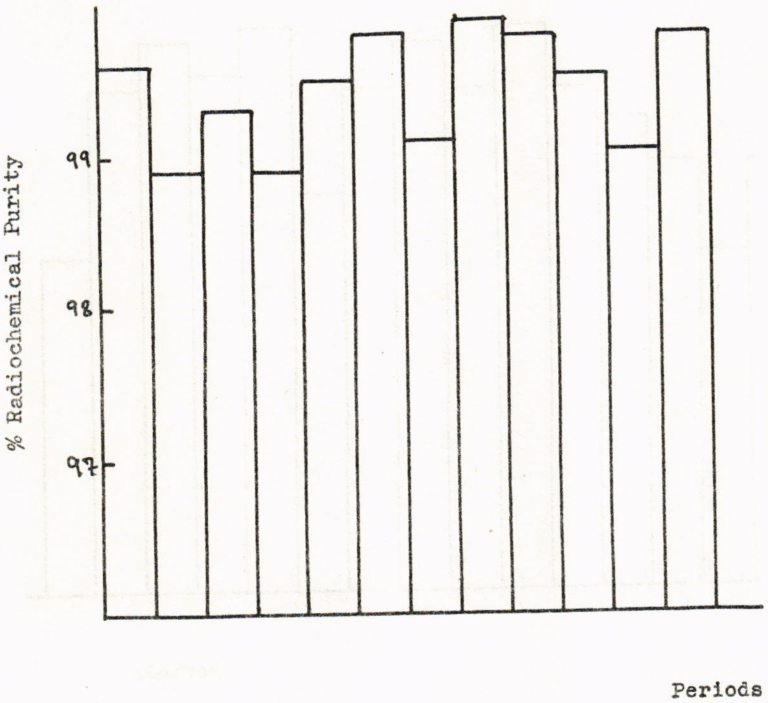

Fig. (3). A histogram showing radiochemical purity of different batches of Triolein-I-131 during 4 years.

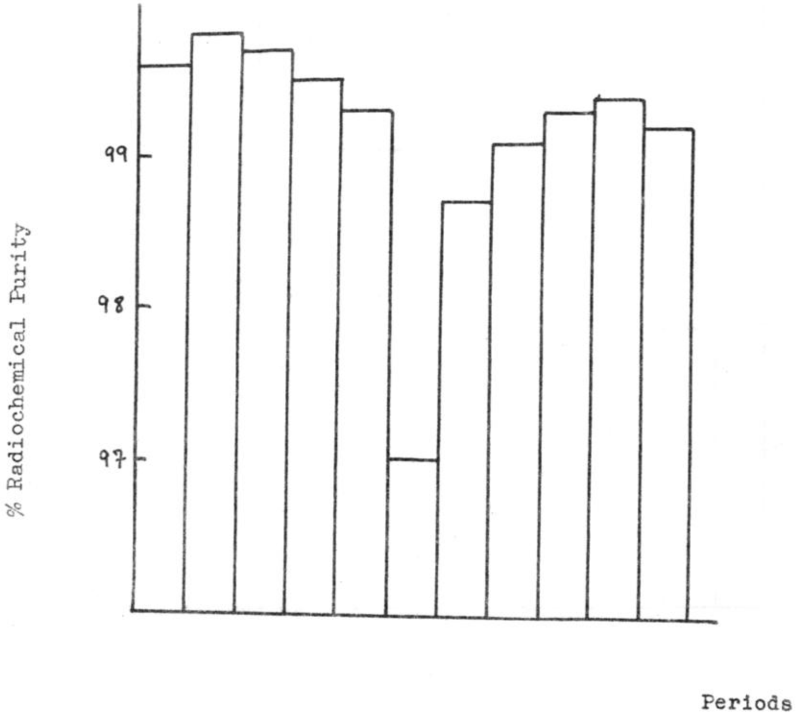

Fig. (4). A histogram showing radiochemical purity of Tc-99m eluates during production of Mo-99-Tc-99m generator for 4 years.

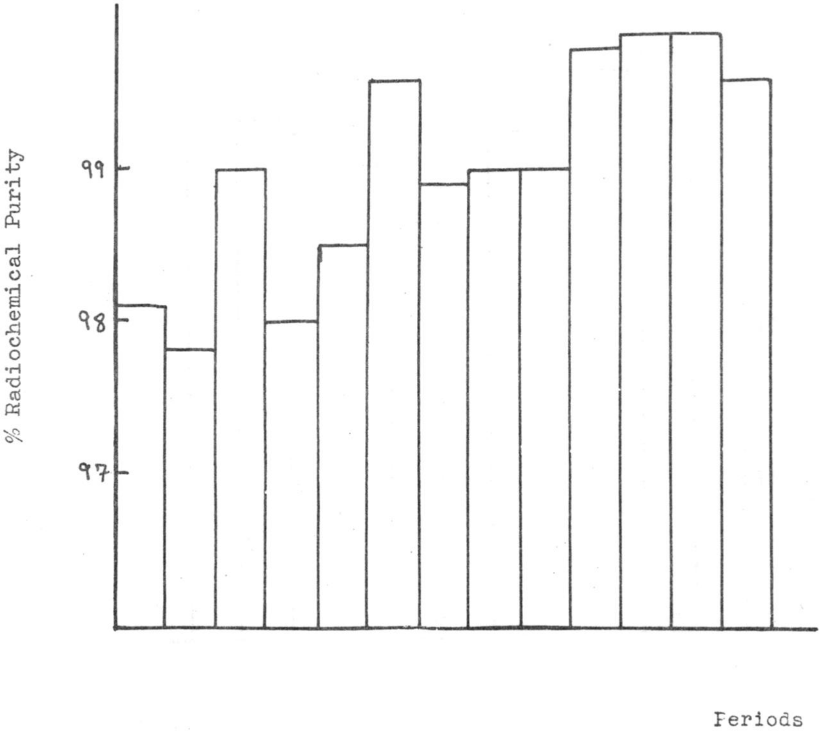

Fig. (5). A histogram showing radiochemical purity of colloidal Au-198 solution during 4 years.

SYNTHESIS OF ACYLATED 2-HYDROXY -D-RIBAL

F.B.I. Al-Bandar and Salman A.S. Al-Janabi*

INTRODUCTION

Recently, various reactions have been accomplished for the preparation of 2-hydroxy -D-glycals as resonably active precursors for wide synthesis of Nucleosides through addition reactions [1, 2]

Acylated 2-hydroxyglycals are usually prepared by the base-catalysed trans-elimination of hydrogen halide from polyacylglycosyl halides in which the halide and the 2-acyloxy group are cis related [3] . Diethylamine or sodium hydroxide in inert solvents were used as basic medium for the elimination process but with low yield 4 .

Rao and Lerner have introduced the use of the strongly basic 1,5-diazabicyclo(5.4.0) undec-5-ene (DBU) which has shown to be an exellent base for such elimination reactions, giving yields far superior to those obtained using bases such as diethylamine [2]. The use of DBU have greatly improved the yield of the above mentioned unsaturated sugar as it has been applied with modification in a mixture of DBU / LiBr in HMPTA on various polyacylglycosyl halides.

2,3,5-tri-O-acetyl-D-ribofuranosyl bromide (1) was treated first with DBU in DMF but no unsaturated sugar was detected, instead, deacetyaltion took place apparantly due to the fact that the bromide to be eliminated is cis to the hydrogen at C_2 which needs prolonged treatment that definetly leads to the hydrolysis of the highly

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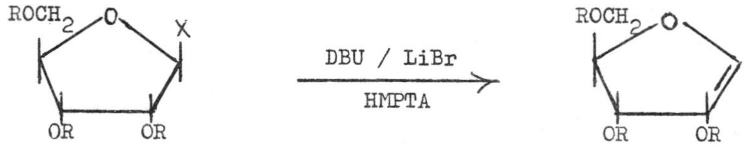
unstable furanohalosugars. The presence of free halide ions in the solution would lead to an equilibration between the α and the β isomers of the halosugar which would create a reasonable concentration of the halosugar that would lead to the formation of the olefine, therefore the halosugar was treated with DBU in the presence of LiBr and hexamethyl phosphoric triamide (HMPTA) which afforded higher yield of the olefine (5) due to the presence of Lithium bromide hexamethyl phosphoric triamide complex as a highly soluble source of the halide ion.

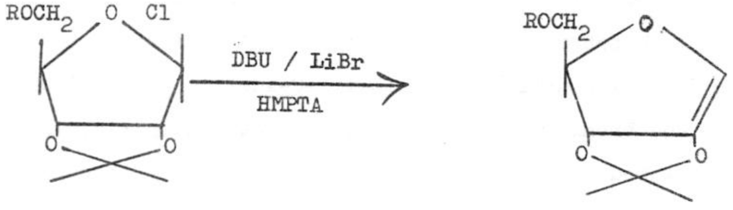
Compounds (2) and (3) were treated under the same conditions giving similar results affording (5) and (6) respectively with no traces of side products due to hydrolysis.

The idea of neighboring group participation that could affect the above reactions was taken into consideration as compound (4) was treated with sodium hydroxide in 1,2-dimethoxyethane and DBU yielding (7) [5]. Complete elimination of all ester groups in the starting material was also studied by introducing an isopropylidene group on C_2, C_3 and protecting C_5 hydroxyl group with either trityl group (8) or tosyl group (9) affording (10) and (11) respectively [6,7,8].



1: R = Ac , X = βBr
2: R = Ac , X = βCl
3: R = Bz , X = βBr
4: R = Bn , X = βBr

5: R = Ac
6: R = Bz
7: R = Bn



8: $R = Tr = Ph_3C-$
9: $R = Ts = CH_3C_6H_4SO_2-$

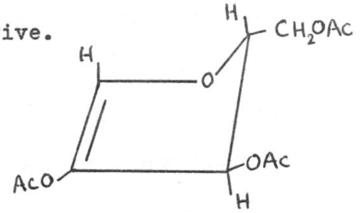
10: $R = Tr$
11: $R = Ts$

RESULTS AND DISCUSSION

Several reactions have been made for the synthesis of unsaturated hexoses but little has been done on the corresponding pentoses [1,2,4]. Pentoses are the major sugar unit in many naturally occuring compounds and especially in the most important nucliec acids RNA and DNA and the hope to create an easily adding centre (double bond) in a pentose would furnish a wide path for the synthesis of such vital compounds. One of the most important methods for the preparation of unsaturated compounds is through dehydrohalogenation of the right halocompound, such reactions were smoothly carried out on pyranosides [1, 2]. Furanosyl halides are much less stable than the corresponding pyranosides but reactions has been carried out successfully to yield the right glycosyl halide [9 , 10] .

DBU in DMF was used primarily on the -substituted poly-acylribosyl bromides and chlorides with no formation of the unsaturated product apparantly because of the cis relationship between the halogen and the hydrogen to be eliminated and the great tension arising from flipping the molecule to the right configuration.

A mixture of DBU and LiBr in HMPTA producing Lithium bromide hexamethyl phosphoric triamide complex as the eliminating agent for dehyderohalogenation of 2,3,5-tri-O-acetyl- β -D- ribofuranosyl chloride and bromide (1) (2) was used successfully yielding 31% of the unsaturated sugar which was identified clearly through C,H analysis. I,R and N.M.R. spectrum showed clear peaks for the right groups and hydrogen atoms in the expected molecule (5) with configuration (12) as shown in tables 1 and 2. Chemical test for the presence of the unsaturated double bond in both dilute $KMnO_4$ and Bromine water was positive.



(12)

Table (1) showing selected streching bands for compounds 1,2 and 5 cm^{-1}

	C - X	C=O (ester)	C=C	H-C=C
Compound (1)	320	1745	-	-
(2)	280	1745	-	-
(5)	-	1745	1645	1665

Table (2) showing selected chemical shifts for compounds 1,2 and 5 δ

	H_1	H_2	H_3	H_4	H_5
Compound (1)	5.40	4.9 -----	5.3	4.10	3.9
(2)	5.16	4.8 -----	5.1	4.30	-
(5)	6.22	5.3 -----	5.4	4.18	-- 4.5

EXPERIMENTAL

Dehydrobromination of 2,3,5-tri-O-acetyl- β -D- ribofuranosyl bromide:

Hexamethyl phosphoric triamide (20 ml) was added to a suspension of lithium bromide (3.8 g.) in toluene (100 ml). The mixture was warmed and the resulting solution was evaporated. The residue was dissolved in DMF (10 ml.) and the bromide (1) (3.5 g.) was added followed by DBU (2 ml.). T.L.C. indicated the presence of two components. The mixture was worked up after 12hrs. giving a brown syrup (5g.) which was chromatographed on silica (350 g.). Elution with benzene gave a fraction (0.85g.) which, on crystallisation from ethanol, gave 2,3,5-tri-O-acetyl-2-hydroxy-D-ribal (5), (0.55g., 16.7%), m.p. 105-107°, $(\alpha)_D^{28}$ - 3.75 (chloform).

I.R.data: ν_{max}^{Nujol} : 3480·cm^{-1} (sharp) due to (OH) group of water of crystallinztion.
3020 cm^{-1} (m) ethylenic H.
1745 cm^{-1} (s) due to ester group ($OC-CH_3$).
1645 cm^{-1} (w) due to olefine ($C=CH-$)

N.M.R. data: at ppm (δ) 6.22(1-proton, singlet, H_1) 5.4 (1-proton, doublet, H_3) 4.18-4.5(2-protons, multiplet, H_4, $2H_5$)

Anal. Calc. for $C_{11}H_{14}O_7$	C,51.16%	H,5.42%
found	C,49.33%	H,5.67%

Elution with (benzene:methanol, 8:2) gave a fraction (lg.) contained a mixture of first fraction and both second and third fractions which was further purified.

The third fraction (0.5g., 16.4% yield) was a syr p product and identified as 2-O-acetyl-2-hydroxy-D-ribal, $(\alpha)_D^{28}$ -50°(in $CHCl_3$).

I.R. data: Nugol ν_{max} 3450 cm^{-1} (s) (OH) group.
3090 cm^{-1} (m) ethylenic H.
1745 cm^{-1} (s) ester group (C=O)
1665 cm^{-1} (m) olefinic (C=C)

Anal. cals. for $C_7H_{10}O_5$ C, 48.27% H, 5.74%
found C, 47.92% H,5.90%

Reacetylation of fraction three increased the overall yield of olefinic sugar (5) to (33%).

2,3,5-tri-O-acetyl-2-hydroxy-D-ribal (5):-

A solution of 2,3,5-tri-O-acetyl-D-ribofuranosyl chloride (2) (3.5g.) in DMF (8ml.) was treated with Lithium bromide (3.2g.) and HMPTA complex (20ml.) followed by DBU (1ml.).

The reaction mixture was left at room temp. for (14) hrs. T.L.C. indicated the presence of two components with different R_f values.

The reaction mixture was worked up as usual to give a colorless syrup (2g.) which was chromatographed on silica gel (100g.) and then eluted with benzene : methanol 8:2.

The column yielded first a clean fraction of 2,3,5-tri-O-acetyl-2-hydroxy-D-ribal (0.8g. 31% yield) m.p. 107-108° $(\alpha)_D^{28}$-32 in $CHCl_3$. The compound decolorized bromine water and dil. $KMnO_4$ soln.

Anal. calc for $C_{11}H_{14}O_7$, C,51.18% H, 5.42%
found C,49.91% H, 5.60%

I.R. data $\nu_{max.}^{Nujol}$ No absorption for (OH) group
No absorption for C-X group
1645 cm^{-1} olefinic (HC=C)
1745 cm^{-1} acetyl carbonyl

N.M.R. data: at ppm (δ) 6.22 (1-proton, singlet, H_1)
5.4 (1-proton, doublet, H_3)
4.18-4.5 (3-protons, multiplet, H_4, $2H_5$)
2.1 (9-protons, triplet, CH_3 in Ac)

The second fraction (0.4g.) was a mixture of the two components, and the third fraction which was eluted (0.6g.) was identified as 1,2,3,5-tetra-O-acetyl-β-D-ribofuranose which apparantly has been formed via hydrolysis of the halide ion followed by trans esterification.

5-O-trityl-2,3-O-isopropylidene-2-hydroxy-D-ribal (10)

A solution of 4-O-trityl-2,3-O-isopropylidene-β-D-ribofuranosyl chloride (8) (0.2g.) in DMF (2ml.) was treated with lithium bromide (0.2g.) hexamethyl phosphoric triamide (1ml.) complex followed by DBU (0.1ml.). The reaction mixture was left at room temp. for (10) hrs. T.L.C. indicated the presence of three components. The mixture was worked up as in the usual way to give a brown syrup (1g.) which was absorbed on silica gel column (60g.) Elution with benzene:methanol 8:2 gave first a mixture of two components of triphenyl phosphine and its oxide.

The second fraction (0.05g.) (27.7% yield) was 5-O-trityl-2,3-isopropylidene-2-hydroxy-D-ribal (10), m.p. 80-85°, $(\alpha)_D^{28}$ -45°.

I.R. data: ν_{max}^{Nujo} No absorption for OH group

3060^{-1} for ethylenic hydrogen

1670 cm^{-1} for (HC=C)

1600 cm^{-1} for aromatic protons

1390, 1380 cm^{-1} for (gem-CH_3)

N.M.R. data: at ppm (δ) 6.98-8.1 (15-protons, multiplet, aromatic protons).

6.32 (1-proton, singlet, H_1)

4.7-3.65 (4 protons, multiplet, H_3, H_4, $2H_5$).

1.5, 1.25 (3-protons, two singlets, (CMe_2).

2.45 belonged to reagent DBU.

5-O-Tosyl-2,3-O-isopropylidene-2-hydroxy-D-ribal (11):

A solution of 5-O-tosyl-2,3-O-isopropylidene-β-D-ribofuranosyl chloride (9) (0.1g.) in DMF (1ml.) was treated with Lithium bromide (0.1g.) HMPTA (0.5ml.) complex followed by DBU (0.05ml.).

The reaction mixture was left to stand at room temp. for (10) hrs. T.L.C. indicated the presence of three components. The mixture was worked up as usual to give a brown syrup (0.4g.) which was adsorbed on a silica gel column (25g.) Elution with bezene:methanol 8:2 gave first a mixture of two components of triphenyl phosphine and its oxide.

The second fraction (0.02g.) (23.5% yield) was the D-ribal derivative (11).

I.R. data: Film $\nu_{max.}$

No absorption for (OH) group

3080 cm^{-1} for aromatic protons.

3020 cm^{-1} for ethylenic hydrogen

1675 cm^{-1} for (HC=C)

1580 cm^{-1} for (aromatic)

1380, 1370 cm^{-1} for (CMe_2)

1310, 1270,1200, 1180, 1160, cm^{-1} for (sulfonyl).

REFERENCES

1. N.A. Hughes, Carbohydrate research, 25, 242-245, (1972).
2. D.R. Rao and L.M.Lerner, Carbohydrate research, 19, 133-134 (1971).
3. R.J. Ferrier, Advan. Carbohyd. Chem. 20, 67, (1965); 24, 199, (1969).
4. M.G. Blair, Advan. Carbohyd. Chem. 9, 97, (1954).
5. H.P. Albrecht, D.B. Repke and J. G. Moffat, J. Org. Chem., 39, 2176-2182, (1974).
6. P.A. Levene and R.S. Tipson, J. Bio. Chem., 115, 731, (1936).
7. G.R. Parker, Method in Carbo. Chem., II, 168, (1963).
8. J.B. Lee and T.J. Nolan, Can. J. Chem., 44, 1331, (1966).
9. R.A. Earl and L.B. Townsend, J. Cabohydrates Nucleosides & Nucleotides, (1,2), 177-178, (1974).
10. R.S. Klein, H. Ohrul and J.J. Fox. J. Carbohydrates Nucleosides & Nucleotides, (1,3), 265-269, (1974).

SEISMO-ENGINEERING GEOLOGICAL STUDY AND PROPOSED SEISMIC INSTRUMENTATION OF HIGH DAMS AT SULIMANIYAH GOVERNORATE, N.E.IRAQ

PART (I) SEISMO-ENGINEERING GEOLOGICAL STUDY

M. Mashkour *

ABSTRACT

The large earth Derbendikhan dam (128 mt) and Dokan concrete dam (116.5 mt) represent a notable important type of seismic and engineering hazards evaluation problem, not only the dams in themselves a relatively expensive projects, but are intimately involved in the whole economy, through power generation, flood control, irrigation, etc. In addition structural failure of these dams may lead to a major disaster because large population may be exposed to sudden flooding.

Since the construction of these two dams and full impounding of their reservoirs almost 18 years ago, several engineering and seismic problems were met. The purpose of this paper is to shead light on these problems, discussing and evaluating them.

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Information gained from this study will be of value during construction of future dams in the geologically complicated and relatively seismic parts of North and North East of Iraq.

(1) INTRODUCTION

The evaluation of the engineering and seismic conditions of sites where dams are founded, and study of their response to the various engineering-geological and seismic effects, particularly after the reservoir full impoundment will certainly promote many valuable informations. Such information are quite useful and helpful to civil and engineering-geological personals helping them when choosing a dam site or even the type of the dam to be constructed in the geologically complex and relatively active seismic provinces of north and north east of Iraq. In addition to the danger from natural earthquakes, the danger apparently related in some way to reservoir loading behind the dam. Thus the risk from induced seismicity must for the time being, be considered for all proposed large dams in the area.

(2) REGIONAL SETTING (LOCATION TOPOGRAPHY AND CLIMATE)

Sulimaniyah governorate lies in the mountainous region of the north eastern Iraq. Boundaries extended approximately from lat. 34° 50' N to 36° 20' N and from 44° 55' E to 46° 20'E.

It lies at an average elevation of approximately 3000 ft above sea level. The governorate lies in two physiographic provinces, the fold province which is characterized by a series of north west - south east trending ridges, progressively becomes higher towards the north east till it end abruptly along a line which marks the emergence of the first great thrust fault. North and north east of the line (thrust fault), the topography as well as the geology, becomes less regular and more complex where rugged mountains and relatively narrow canyons and valleys are the dominant. Well back in the fold province, there are two plains, the Sharazoor and Rania-Qala-Dizeh plains.

The structural ridges force the cyclonic storms from the west to rise, thus causing a large increase in precipitation in the governorate compared to the southerly and central areas of Iraq, Hassan and Mashkour [1] .

(3) HISTORICAL GEOLOGY

During Triassic, Jurrassic, Cretaceous and Eocene time, the area was submerged, and a considerable thickness of marine sediments was deposited. The character of sediments varied with depth of the sea, proximity to land and climate, but in predominantly calcareous, INOC [2] . Disregarding probable tilting of pre-cretaceous strata, major distrophism began in upper cretaceous time. Large scale compressional movements, culminated in pliocene and lasted until late pleistocene time. These movements compressed the mesozoic and early tertiary sediments into great folds and nappes, with associated thrust faulting raised them as a new land mass. By early pleistocene the present north west-south east alignments of structures in the zone of normal folding was well established and considerably eroded. Continued intermittent uplift of the region during pliestocene epoch variously estimated as beginning one million to two millions years ago and ending approximately 30,000 years ago. These uplift help generating deep gorges in the province. Pauses in uplift possibly associated with a local depression, allowed Rania and Sharazoor plains to be filled with alluvium and becomes a well-graded plains. Fig.(1) shows the cretaceous sediments formations crop out extensively in the high folds and nappe zone physiographic provinces. Metamorphic sedimentary and some Metamorphic-Igneous rocks are especially prominent in the nappe zone of faults.

(4) TECTONIC AND STRUCTURE

The regional interaction between the Arabian, Turkish and Iranian plates due to the movement of one of the major orogenic period of the earths crustal deformation has produced a pattern of deep seated block faulting of NE - SW direction, and as a result of the compressional phases of the Alpine orogeny a series of a symmetrical anticlines and synclines trending NW - SE increasing in amplitude toward the north east see Fig. (2) by Buday [3] . The folds are accompanied by major faults which are

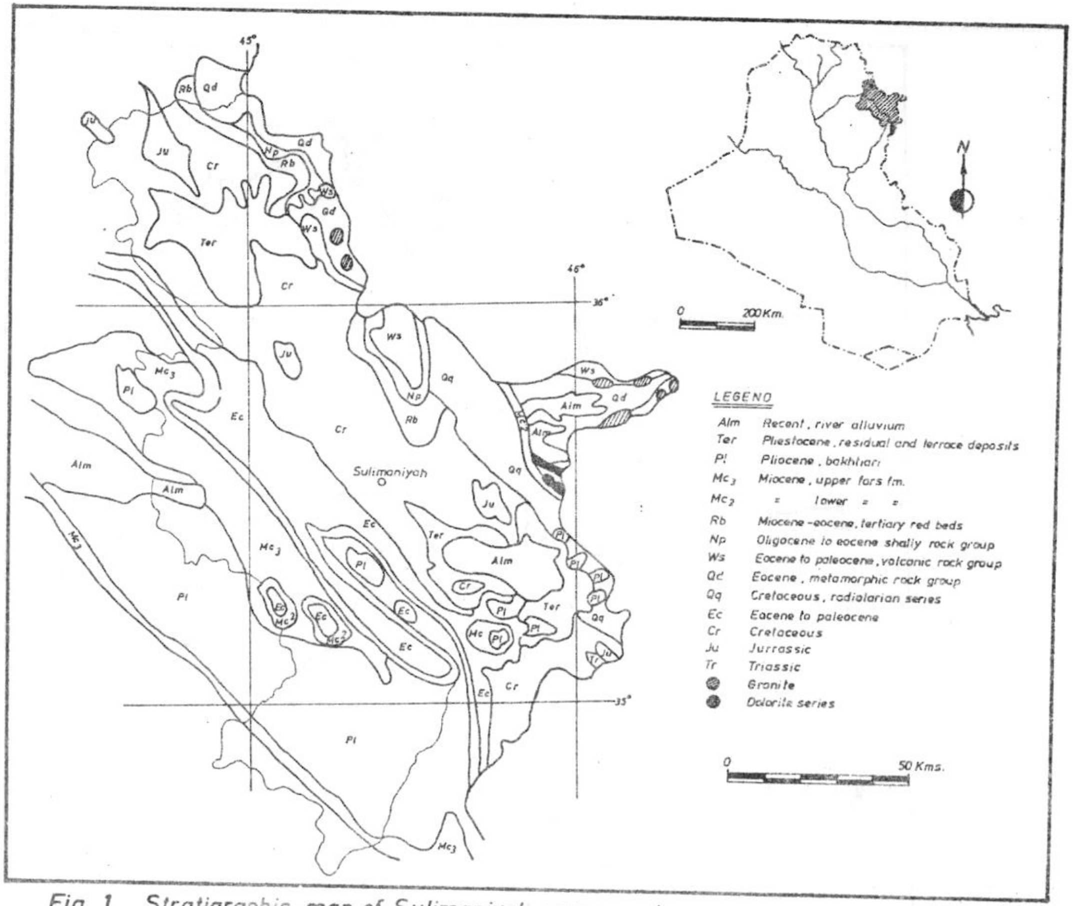

Fig. 1 . Stratigraphic map of Sulimaniyah governorate .

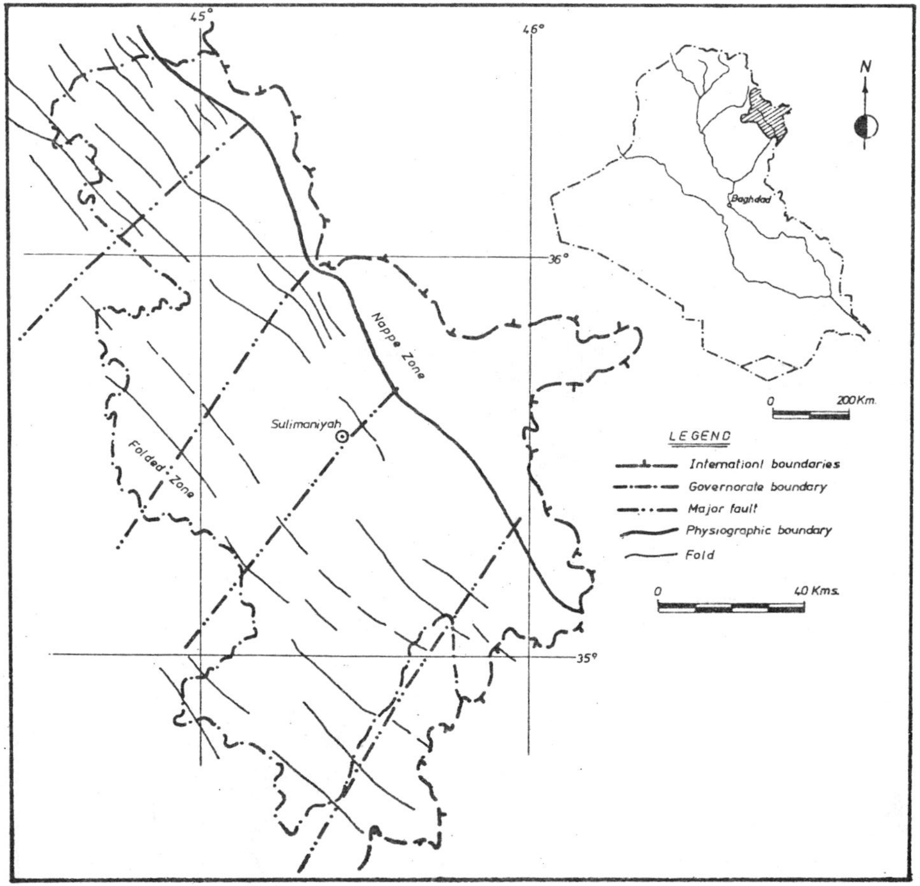

Fig. 2. Tectonic map of Sulimaniyah governorate.

exposed as either crestal collapse faults or cross axial faults with little displacements. Folding was accompanied by thrust faulting (nappe zone). The directions of thrusts being south west.

4.1- Dokan reservoir and dam site structure.

The structure of the reservoir is shown in Fig. (3) by Binnie et al [4]. At the dam site, the cretaceous rocks are folded into a symmetrical anticline. Upstream of the anticline is followed by a steeply dipping thrust fault, see Fig. (3a). There is no really major dislocation or faulting in the structure of the site. Most faulting has taken place along major joint dislocation. Another important dislocation is the rather confused and localized block faulting immediately upstream of the left abutment position, see Figs. (4a) and (4b).

4.2- Derbendikhan reservoir and dam site structures.

The structure of the reservoir see Fig. (5) by Harza [5] shows the major faulting. The dam site is on the southwest limb of a long NW- SE trending anticline which forms the anticlinal mountain known as the Beranand Dagh. Fault associated with this transverse fold follows the course of the river as shown on the geologic map and geologic section see Figs (6a) and (6b). It extends upstream of the dam axis where it passes a zone of minor disturbances with some shearing and brecciation. The fault itself does not continue under the dam foundation. An associated

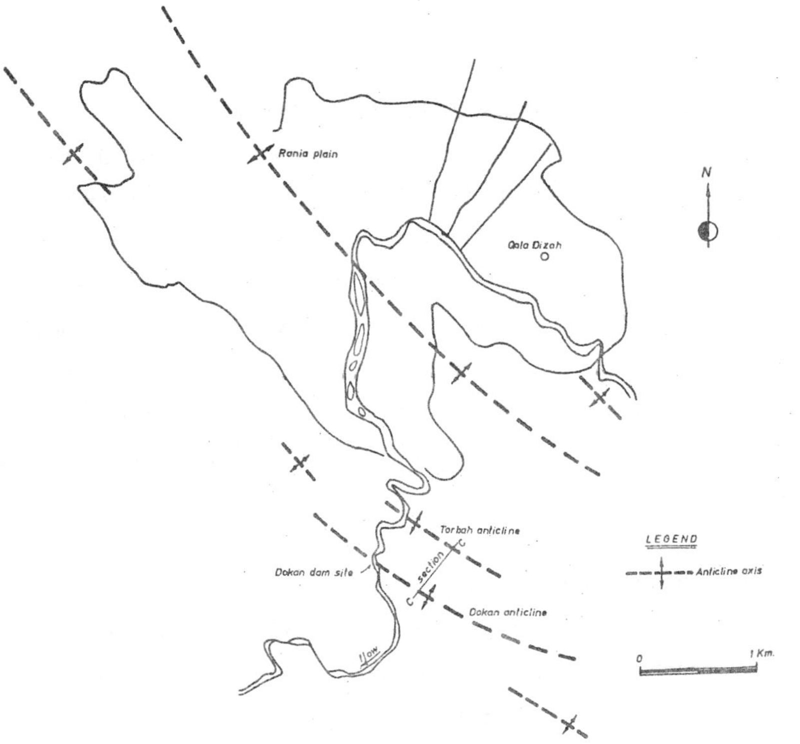

Fig. 3a. Structural map of Dokan reservoir.

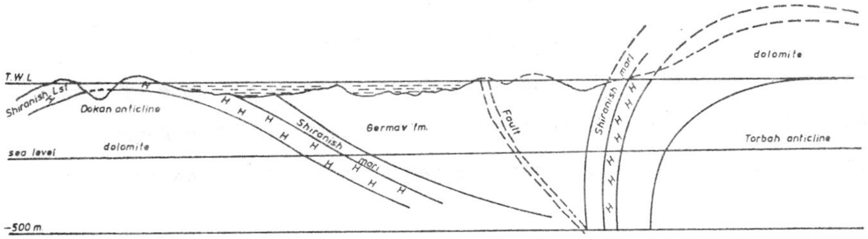

Fig. 3b. Geologic section through Dokan-Torbah anticlines.

Fig 4a. Dokan dam site structure.

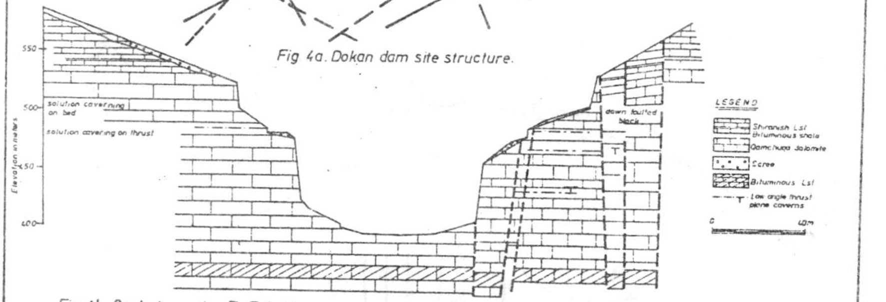

Fig. 4b. Geologic section E–E looking upstream on axis of dam.

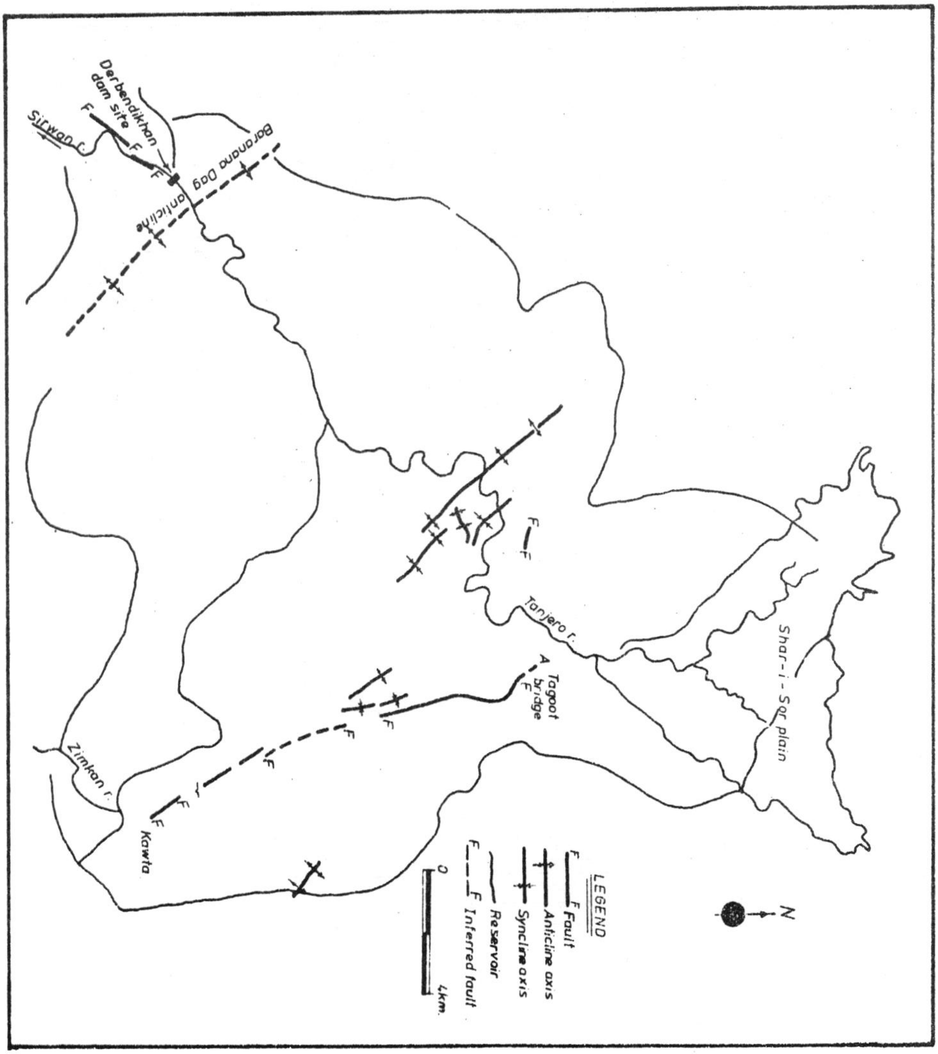

Fig. 5. Structural map of Derbendikhan reservoir.

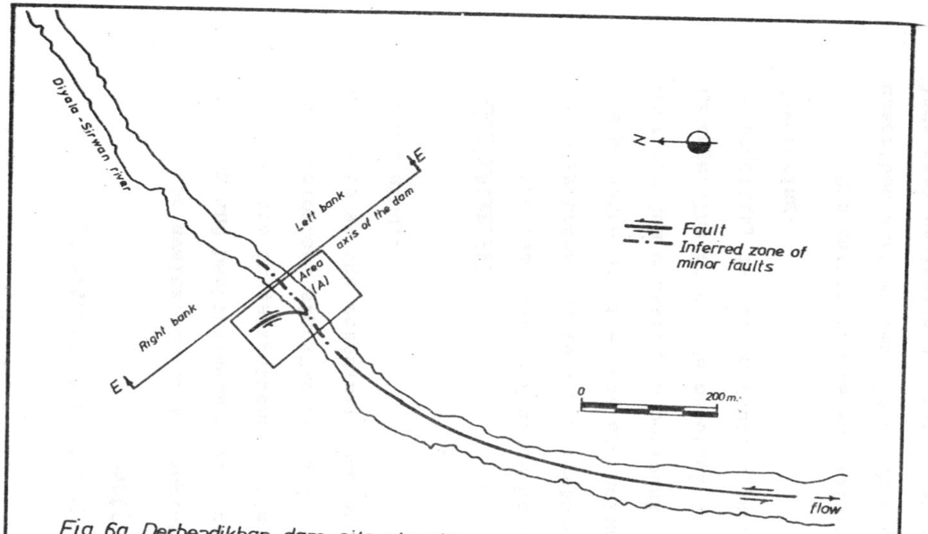

Fig. 6a. Derbendikhan dam site structure .

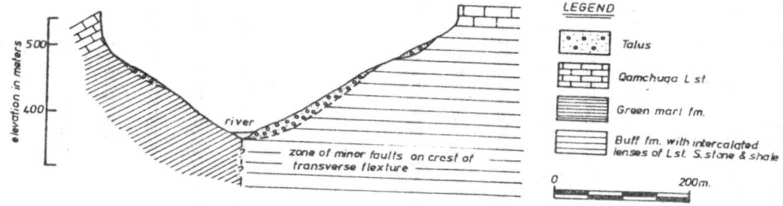

Fig. 6b. Section E - E looking upstream on axis of dam.

auxiliary thrust fault with a displacement of about ten meters on the right abutment in the Buff green marls Fms. The degree of brecciation along the trace of this fault is negligible.

(5) EVALUATION OF THE ENGINEERING-GEOLOGICAL CONDITIONS

For evaluation of the engineering-geological conditions of Dokan and Derbendikhan dams, results of surface and subsurface site investigations of the rock conditions, competence, hydrogeological significance and more particularly the problem of faults at the reservoir area and dam sites has to be taken in the study.

5.1- Dokhan dam.

The dam base is founded on dolomite. Approximately horizontally bedded shale and limestone higher up the valley sides. The presence of limestone and dolomite upstream and downstream from the dam constitutes obviously the most important risk of leakage. The rock as a material is water tight. However its permeability is due to faults, joints and to its intensive fracturing.

The net of faults and joints affecting the dam site is described just in section 4. The system of faults cutting the left bank peninsula against which the left abutment of dam thrusted is the most dangerous one because it constitutes a means of direct communication between downstream and upstream, this is why it was decided to make the area into a solid mass by cement-sand grouting. Another major problem was that of securing water tightness in the reservoir from a gorge known as Gulneri gorge which runs parallel to the river at a distance of 2 km, D.G.D.R. reports [6 - 8]. The state of grouting is shown in Fig. (7) by Walters [9].

Impounding of reservoir was started Feb. 1959. After completion of the filling, it was found that quite large quantities of water leakages through the rock at the site and distances particularly at the right bank of the dam.

It was found that there are two courses of leakages, Al-Imam [10], the first at the Gulneri gorge location at distance of 3 km NW of the dam. There, the rock are dolomite exposed to the air and shows the water of the reservoir reaches the dolomite and may easily find its way along 2.5 km to Dokan gorge through more or less open cracks parallel to the axis of the anticline and due to its bending effects.

The dolomite outcrops in this gorge at an elevation of about 470 mt and the reservoir at top water level enters the gorge for about 500 mt. Therefore as a measure it was decided, Al-Imam [10] to extend the grouting curtain on the right abutment to reach the considerably impervious marl, see Fig. (7). The other source of leakage is the left penensula which form the left dam abutment. It is the shortest path for water to

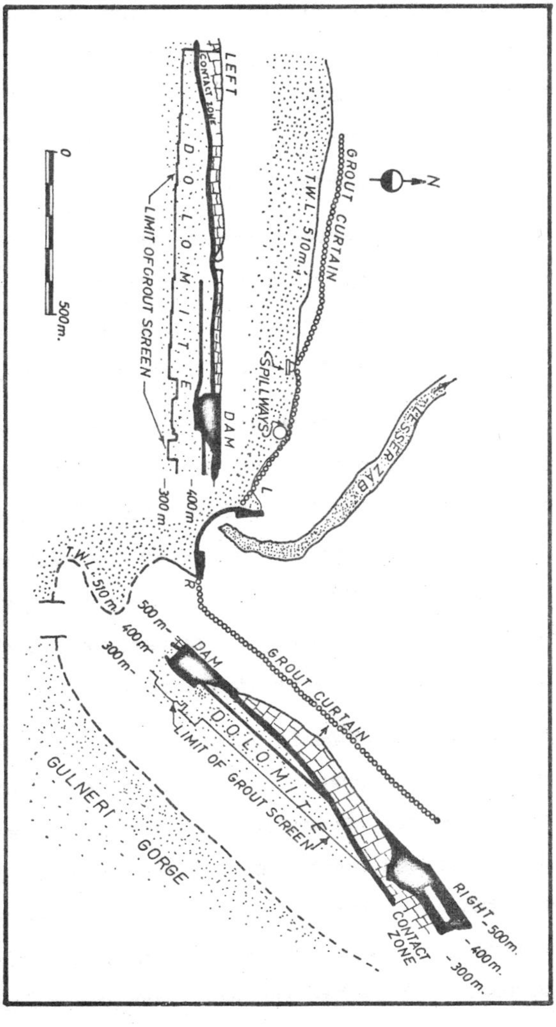

Fig.7. Grouting programm at Dokan dam (After Walters, 1962)[9].

percolate from the reservoir to downstream. There on the left side of the cliff just downstream the dam, a more or less continuous line of cavities are shown. However no leakages from this thrust plane was apparent above river level, Nonveller and Sabarly [11] . For remedy, an extension of the grout curtain was carried out to pass through the northern edge of the penensula to cutoff the perculating water leakages from the reservoir. In addition grouting was also designed to different parts of the penensula for site strengthening. The seepage problem into the right and left abutment continue even after the new additional grouting mentioned above. Nonveller and Sabarly [11] have studied the case in order to prove necessity of any other grouting works but concluded the followings :

1. There is no immediate danger from the leakages that appear far away downstream of the dam either on the left bank or in the right bank grouting gallery.
2. The only immediate danger would be high uplift pressures in the abutment of the dam and in the banks of the gorge just downstream of the dam, especially in the left abutment.

5.2 - Derbendikhan dam .

The dam is founded on the shale members of the Buff formation which form a very good barrier against leakages under the dam. The intervening of sandstone and limestone are relatively impervious but grouting were made to complete the seal between the shales and the rock fill dam. However the characteristics of the Buff formation present great difficulty, since it is heterogeneous in character. It consists of lenses of limestone, sandstone, and shales which vary in characteristics throughout the formation. The foundation in the stream bed are further complicated by the minor shearing and brecciation of the fault which follows the course of the river and by the thrust fault exposed on the right abutment explained in section 4., and showed in Figs.(6b) and (8). Geologic reconnaissance indicates that these two faults have not been active on recent times, and have zone of brecciation as indicated by the cores of drill holes carried out under the river. More important is the fault zone 10 - 20 mt encountered the small thrust fault. It is that part of foundation place that water was outbreaked which have caused several difficulties experienced during compacting the contact layer of the clay core and grouting. Samples of this water were analyzed, Coyneet and Bellier [12] have showed to contain compounds of 174-240 mg/Liter. This water believed to come from deeper strata not the ground water coming either from surface or from percolation due to low head in the basin upstream from the coffer dam. The reasons to believe so are stated here based on the results by Nonveiller and Sabarly [13] :-

1) Only high piezometer readings (1962-1974) were established at stations 310 and 328, both reaches the thrust fault zone along the right bank abutment, see Area (A) of Fig. (6a).

Fig. 8. Geology of Derbendikhan dam right abutment.

2) Inspection of the observation holes on the right bank gallerly showed that water with sulphuric odour and warmer than the ambient temperature was flowing out from the observation holes (328), see also area (A) of Fig. (6a).

3) The water contained chips of marls, it was turbid and of grayish color., indicating the erosional phenomena during reservoir operation in the thrust fault zone on the right abutment of the dam. Therefore the suggestion here, that there is some upstream connection in the fault zone of the right bank between the mineral water rising from greater depth in the fault at the right abutment and the right abutment and the water in the reservoir, i.e., there is deep circulation of water or a hydraulic continuity between reservoir water and deeper layer. The significance of this phenomena will be discussed later in section (7IV).

Leakages under the earthern embankment of Derbendikhan is very dangerous since the dam was built on soft material of the Buff formation which is liable to be scoured out and it is itself also vulnearable to the inflow of water. Therefore the check to see whether the subsoil condition region of foundations have changed since the reservoir first filled in 1962 is of atmost importance. Correlation between the piezometers readings for the period 1962-1974 and the relative lake levels as well as the piezometers level ratio, and discharge ratio at different reservoir levels were made by Nonveiller and Sabarly [13]. They have concluded that apparently no erosion phenomena developed during the reservoir operation in the fault zone of the dam foundation or any leakages or other unusuals events. However it must be realized that even high leakages might go unnoticed in the absence of an leakages monitoring system.

At Derbendikhan dam site, the massive activation of landslides Fig. (9) represents another significant potential engineering hazard to safety of the dam. This slide has long history early noticed in the beginning of the construction in 1956, which have caused the dam designers to modify the dam design. The slide is still continuing uptill now. Generally speaking the slide, is a slow motion movements of a rotational type or more commonly, of creeping movements which speed up with the speed of reservoir level lowering. Some available literatures on the slide [14 - 18] were studied, analyzed and verified by the author close inspection of the slide had lead to the following conclusion:

The landslides are directly related to the marls of the anticlines of Bernand Dagh that runs transversally upstream that has been cut open by erosion. In this way the originally stressed marls (being in the heart of the anticline) are now under severe decompression and are particularly unstable. Also the reservoir that has been saturating 100 mt of marls for about 18 years, creating a totally new geotechnical conditions. Thus

Fig. 9. Photograph of the sliding area at Derbindekhan dam.

resulted in an intensification of the already common phenomena in the specific area. The situation of unstability is more aggravated by the presence of the auxialary thrust fault at the right abutment immediately upstream of the dam extending down the river bottom. Also that the soils are resting on steeply dipping beds toward the same direction, see Fig. (8). The acceleration of the process up to the rupture of natural conditions in the restricted area of the anticline, would not only clogging of an intake, but would produce a much more dangerous phenomena i.e. the waves would reach uncommon hights and concentrated energy that could be disastrous for the rockfill dam. Noda [19] found for the limiting case that the elevation of the crest of the maximum wave generated is given by the formula:

$$\eta \text{max.}/d = 1.32(v/\sqrt{gd}) \quad - (1)$$

and the speed of the wave advance (Horizontal component of velocity (vh)) is approximately :

$$Vh = (gd)^{\frac{1}{2}} \quad - (2)$$

where v - The uniform speed of the moving boundary

η - The maximum elevation of the crest above the undisturbed water surface

g - The acceleration of gravity

d - The depth of water reservoir

If large sliding took place at the sliding area of Derbendikhan dam site, a maximum wave will be generated since (d) depth of the reservoir is at maximum in this place. Elsewhere as the main body of Derbendikhan plain is situated well above present river levels, Hitchen [20] , the main storage capacity is in the upper levels and the average depth of water in the plains will not be great. Therefore the main sliding effect is likely to be the vibration of the water-mass.

(6) EVALUATION OF THE SEISMIC CONDITIONS

The consideration of the overall behaviour of complex geologic structure is often of a significance criterion serving to formulate initial probability distributions of seismicity. For instance the complex geological structure north and north east of Iraq which lies within a complex zagros thrust belt itself was resulted by the collossion of the Arabian shield with the Turkish-Iranian plateau. Therefore one may deduce from plate tectonic theory which explain this collossion to expect earthquakes roughly uniformly distributed along this line of collossion just as shown in Fig. (10) compiled from results by Nowroozi [21] and Al-Sinawi and Galib [22] .

The seismic activity is produced by deformation of material in the crustal layer due to shearing stresses set up by the plate collossion. The pressure relief is partly achieved by the flexture deformations of surface rocks of the thick layer of sediments in the anticlines and synclines, which produce in many cases a faulting displacements. These faulting displacements are often

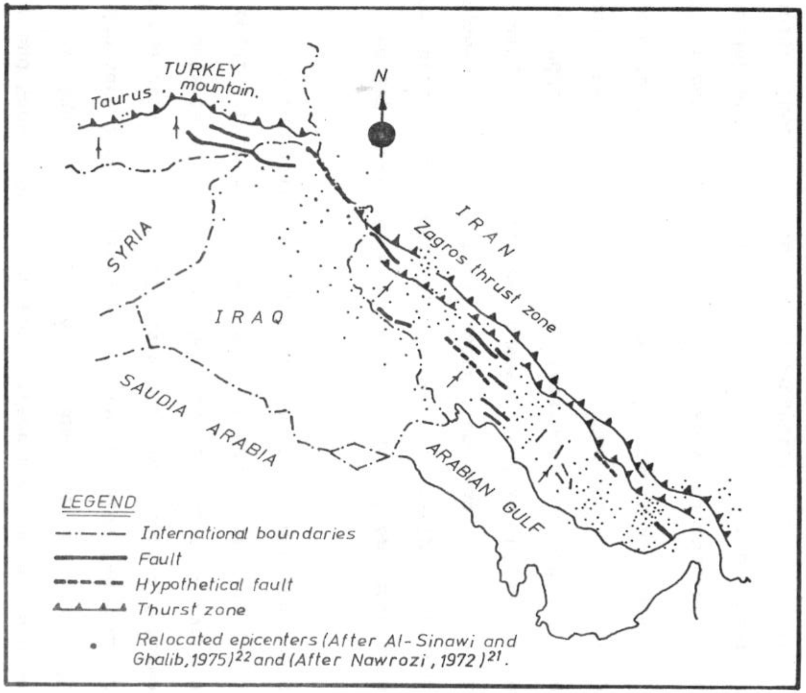

Fig. 10. Map of earthquakes epicenters associated with plate tectonic boundaries .

take place gradually without any sudden breaks and cause an earthquakes generally not felt. Such cases only happen when faults are of small size, shallow, and they cut incompetent rocks. These are called fault creep, Louderback [23] , and Hudson and Scott [24] . Recent surface and underground water supply, irrigation channels in Iraq and Iran Ambrayses [25] , have provided ideal marker of such recent slow faulting or creep and regional vertical movement. The plastic deformation of the materials do not have the same rate of flow everywhere, thus resulting in concentration of stress in certain localities until it overcome the strength of the rocks, and the ruptures occurs.

Relief takes place by means of thrust and breaks faulting in the cores of the anticline or more unusually occasional enlargement of shallow fault occur from time to time. This is causing slightly felt earthquakes, and in the very rare cases, sudden shallow fault may intersect the surface (The breakout phase). The destructive earthquake of penjwin 1946, was associated with surface ground deformation, Ambrayses [25] .

It can be concluded from the above discussion that the area under study is characterized by a certain seismo-tectonic features. These are dealt with separately due to their significance.

1- Most earthquakes in the area are shallow. The importance effect of depth is to increase the distance of the energy source from the clossest engineering structure and thus reduce intensity. Very deep earthquakes do essentially no damage even though they may be felt over a large area. On the other hand occasional small earthquake at very shallow depth may generate anomoulously high accelerations over a limited area. For instance the shallow small earthquake ($M = 4.7$) near Bear valley earthquakes gave an acceleration of 0.69 g at a station near by, Faccioli and Resendiz [26]. Thus it is the very shallow earthquakes that are the principle cause of seismic disasters throughout the world, since there is much release of energy is available per unit surface area and it is those earthquakes on which we must focus our attention.

2- Plastic deformation of the materials do not have the same rate of flow everywhere depending upon stress and depth. Thus resulting in concentration of stresses (producing faults). These faulting are considered as locations of future fracturing since the stresses would tend to be relieved along them rather than in the more sound rock. Had compression is renewed suddently, a removement is taken place along these faults. Hence the recent faulting and fracturing in the rock are in fact to a large degree inherited from the past faulting, but not the very geological past, because the further the back in geologic time one goes, the more irrelevant are relationships to present day tectonic process and common faults. Hence for a better understanding of seismic conditions in the area which is most useful to building codes, is to learn more, region by region of the late Quaternary history of deformation. Allen [27] gave a number of cases, where fault risk associated with earthquakes has been characterized by a history of earlier quaternary and probably Holocene displacements. These very recent displacement are active or potentially active faults, as defined by the U.S. Atomic energy commission Sherard et al [28], that they have one or more of the following characteristics.

A- Displacement at or near the ground surface at least once in 35,000 years or movement or a recurring nature within the past 500,000 years to make it reasonable to anticipate that future displacement could occur within the life of a dam usually 100 years.

B- Instrumentally measured macro-seismicity determined with sufficient precision to demonstrate a direct relationship with the fault.

Therefore seismic site evaluation program need geological and seismological studies to delineate the active or inferred active faults. In view of the absence of local seismic network in the area to verify (B) above, only geological studies can be used for this purpose. The careful and thorough study of reports concerning surface and subsurface geologic features carried out during feasibility stages of Dokan and Derbendikhan dam sites and reservoirs have shown no recent faulting and that existing faulting did not bear evidence of renewed movement. However few faults sites in the foothills folds of Zagros thrust in Sulimaniyah governorate and adjacent areas, Fig. (11) by Ambrayses [25] have been recognized as being active from independent geological and seismological evidences. Strong earthquakes from these active centers can trigger small displacements on other unrelated faults in the area many kilometers distance. For instance, Allen [27] has found for 1968 Borgo mountain earthquake in California ($M = 6.4$) had triggered small displacement (10 - 20 mm) in three other independent faults at distances 45,50 and 70 kms. from the causative fault. As most of the earthquakes in the foothills folds of Zagros are shallow, hence they are formed by elastic rebound as most seismologist believe so, Louderback [23]. Hence the shacking effect should be great near the fault and decrease away from its surface location according to the following formulas by Housner [29] .

$$a = 1230\, e^{0.8M} \, (R + 25)^{-2} \qquad - (1)$$

$$V = 15\, e^{M} \, (R + 0.17\, e^{0.59M})^{-1.7} \qquad - (2)$$

where

a - The gravity acceleration cm/sec^2

v - The ground velocity cm/sec

R - The focal distance to a given point of interest called a station (km).

In respect to above two formulas, the Penjwin earthquake,(July 1946)

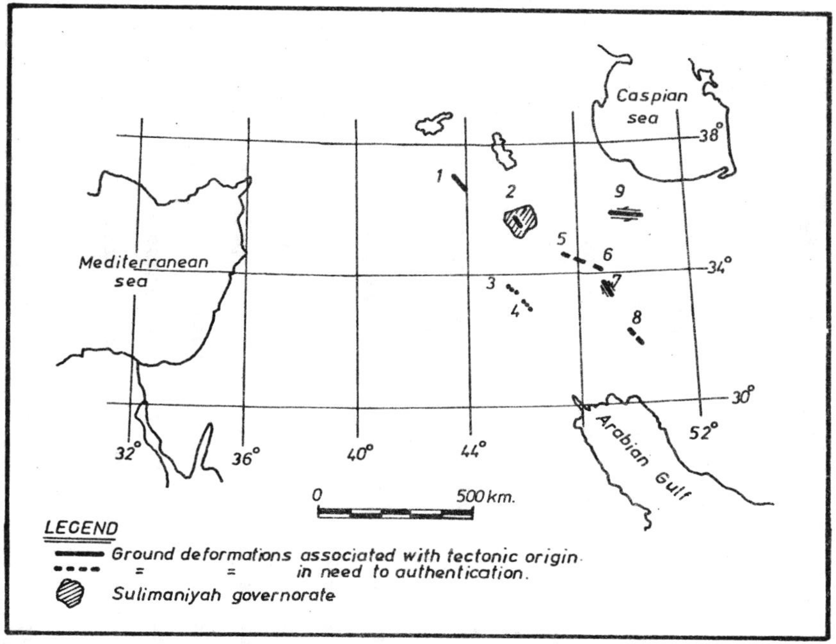

Fig. 11. Faulting associated with earthquakes during the last seven centuries (1,2,3,4 in Iraq), (5,6,7,8,9 in Iran). (After Ambrayses, 1975)[25]

which was almost destroyed the village of Penjwin 100 km. south east of Dokan, but only shacked houses and caused roof fall in Dokan, although no damage was caused there or at Sulimaniyah governorate 50 km. from the epicenter., Tillotson [30] .

(7) FACTORS EFFECTING THE SEISMIC CONDITIONS

For full evaluation of seismic hazard conditions at the dam sites, effect of existing geological and engineering factors at these sites has to be taken in consideration. These are dealt with as follows :

i- Effect of the existing faults

The presence of structural hetrogeneous in rock mass, particularly ancient faults influence the orientation and values of existing stresses. A considerable discontinuous re-distribution of stress takes place in a fault zone.

Photoelastic study of crack under stress by Gzovsky presented in Fig. (12) by Nikolaev [31] shows such redistribution with decrease and increase of stresses in a zone of a crack, which is greatly depend on the form of a crack and on its orientation. With reference to the orientation of the major stresses. Early work by William [32] had showed that the highest stress around crack is a head of and 70° to the right or left of its end. It is in these regions that maximum energy release should be

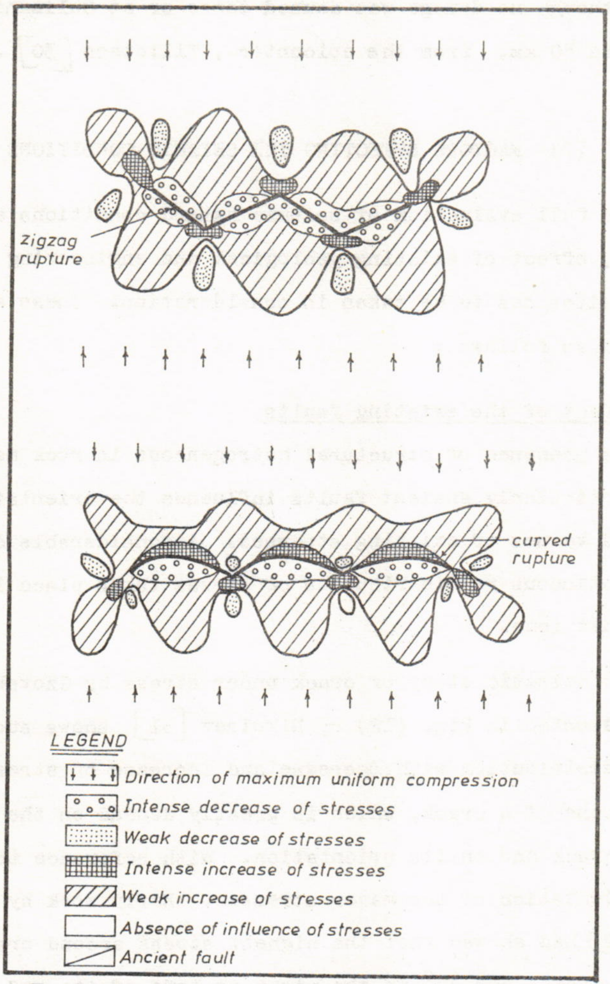

Fig.12. Influence of ancient faults with various orientations shapes on maximum tangent stresses into models. (After Gzovsky in Nikolaev, 1974)[31].

expected when stress is applied. If this knowledge is applied to the structural conditions prevailing in the actual fault in the nature, it would be possible then to realize the effect of fault presence on the incidence of tremors in a particular area. For instance, Amand [33] have actually found that the off-fault areas of high strain energy of the White Wolf fault are a head and 70° to the right or left of its end. The highest stresses due fault will give rise to conditions under which seismic activity is likely to occur when favourable engineering conditions is existing in the vicinity of the fault, Mashkour [34].

A susceptible site of fault effect in the area under study is the area of faults intersection at Derbendikhan dam site, see area (A) of Fig. (6a). Their, the concentration of stresses due to the superimposition faults impacting on each other will give rise to conditions under which a strain energy release may occur, i.e. seismic activity and only in the presence of a triggering stresses. Existence and effectiveness of such triggering stresses in the area will be discussed in VII below.

Effect of folding

The parts of NE of Iraq lies within the tectonically mobile regions in which great thickness of sediments are folded and subjected to different kinds of horizontal

:ense tectonic movements. It is possible that inherent stresses are still existing in these folding which may exceed geostatic stresses (vertical stresses due to depth). Which is a condition of tectonic stresses generating an earthquakes, as was noticed in most seismic active zones of the earth, Hast [35].

The water load in the newly made reservoir of Dokan and Derbendikhan can be of a triggering mechanism for previously high accumulated elastic energy in the fold site of the dam and reservoir. However a point in favour of Dokan gorge site is that the anticline concerned is comparatively gently folded in the region of the site in contrary to Derbendikhan dam site. This reduces the Likelihood or the possibility of shocks originating at or near the Dokan dam.

iii- Effect of ground type

The influence of local ground on earthquakes intensity is the final event of a complex propagation process in which source mechanism and transmission - paths characteristics constitutes the preceeding stages. The seismic oscillation are propagated from focus to station along different paths. Peculiarities of the medium through which seismic rays travel with regard both the elastic properties and discontinuities, apparently produce different terms of ground oscillations. When the shock waves travel through rock, their velocity is relatively high while their amplitude is low but as they move from the bedrock to the overlying soil and their amplitude increases which give rise to a pronounced rise in intensity. This layer can raise seismic intensity only when it consists of loose alluvium on a rock base, Medvedev [36] . With increasing thickness of the layer, resonance properties leading to an additional three to four fold increase in amplitude are manifested. By experiment, Ezio and Rsendiz 26 mentioned that seismic amplifications measured from seismogram of a seismic station located on a consolidated alluvium was several times greater than the amplitude measured for same earthquake seismogram recorded by a station located on bedrock. Therefore it can be concluded that high seismic intensity is expected at dam site where weathered rocks of small thickness of soil covering rock cliffs and valleys. Also high rates of seismic intensity are expected at the Sharazoor and Rania plains where considerable thickness of alluvium based on bedrock, see section 3.

iv- Reservoir induced seismicity

Small earthquakes associated with artificial lakes were explained as due to the sagging of the reservoir basement caused by the load of the water and subsequent crustal adjustments, Westergaard and Adkins [37]. Advanced to this hypothesis Carder [38] thought that water load reactivated the pre-existing faults in the area of Lake Mead, Nevada, U.S.A. The effect of fluid pressure on sliding on faults or joints is obviously of great importance. The criteria for slip would be as follows, Jaeger and Cook [39]

$$|\tau| = S_o + \eta(\sigma_n - P) \qquad - (3)$$

where τ - Shear stress across the plane of fault or joint

S_o - Shear strength

η - Coefficient of friction

σ_n - The normal stress across the plane of fault or joint.

P - Fluid pressure.

The above formula shows that the shear strength of rocks is related to the ratio of the shear along the fault to the normal effective stress across the fault plane. The normal effective stress is equal to the normal stress minus the pore pressure. When the pore pressure increases, the shear stress does not alter, but the effective stress decreases by the same amount. Therefore, the ratio of shear to normal stresses increases. If rocks are under an initial shear stress, as is generally true, an increase in fluid pressure can trigger shear failure and cause earthquakes. The theory of effective stress has been tested experimentally and demonstrated in the case of fluid injection under pressure into deep wells at Denver, Evans [40], and Rangely oilfield, Raleight [41]. However, in most of the reservoirs, including some very large one, no seismic activity has been observed. It is believed, therefore that special geological and hydrogeological conditions are required for the triggering of earthquakes of engineering importance. These are dealt with here due to their importance in explaining possible induced reservoir seismicity in the area.

A. Competence of reservoir basement

Following impoundment of reservoir, the tremors occur under specific geological conditions only and the building of dam does not always produce earth-tremors. Rothe [42] sited the example of the Serre-poncom dam in the French Alps, where the artificial lake is entirely situated on a flexible terrain situated by back soil in which stresses were unlikely to be accumulated. No earthquakes have occurred in the region following reservoir impounding. In contrast to this situation, the Koyna dam (India), reservoir which was on more competent basalt flows, which could have a great amount of Latent seismic energy stored in them and the energy is ready to be triggered by reservoir impounding has actually showed reservoir induced seismicity, Gupta et al [43].

B. Hydraulic continuity

The necessity of hydraulic continuity to deeper layers in inducing the earthquakes in the reservoir areas has been demonstrated by the lake Mead and the Dale example Carder [40] . In the Virgin - Detrital basin of Lake Mead, the hydraulic continuity between the reservoir water and deeper layers is probably banned by impervious very thick deposits of salt and clay. A number of faults which are present beneath this basin, were probably not activated in the absence of hydraulic continuity (note that, the effect of stress due water load for fault reactivation can reach at depth approximately the reservoir width, Gough [44] , and Gough [45] . The seismic activities of the lake Mead area is mostly confined to the Boulder basin were salt deposits have not been formed. Similarly hydraulic continuity to deeper layers has also been inferred in the cases of Koyna (India),Kariba(Zambia-Rhodesia border), and Kremasta (Greece) reservoirs, all of which have showed seismic activities, Harsh and Rastogi [46] . At these dams sites, the presence of hot springs is an indication of the deep circulation of water i.e. hydraulic continuity. Usually reservoir induced seismicity are best assertained by a seismic network adequate for approximate location of these small events. As far as the seismic study at Dokan and Derbendikhan reservoirs are concerned, there is no such small seismic network. Neverthless an attempt to prove reservoir induced seismicity at Derbendikhan reservoir is attempted here :

At 8 P.M, Nov. 27th, 1974 there were three alarming shocks at Derbendikhan dam site, Al-Immam et al [47] , the first shock was the strongest and lasted few seconds and was followed by two other shocks of less strength and duration at one minute and three minutes from the beginning of the first shock respectively. The intensity of the earthquakes were unknown due to lack of seismographs in the area, but the intensity of the first shock was of a sufficient strength to move wall and caused fall of ornaments and fall of two roofs of two houses located at 1.5 km. distance from the dam site.

The small microseismic zone of the termor is evidence of fall-off in its energy with distance from the epicenter. For example it can happen that tremors felt and shock the dam and cause crack, but not felt beyond the village barely of 1.5 kilometer distance from Derbendikhan dam site. If the focus of this tremor, lay in the vicinity of Derbendikhan dam site at some depth assumed 5 km. The length of the path from this focus for a place 1.5 km. (i.e. Derbendikhan village) would be only about 5.5 km. (r_1'). This is a very little greater than the distance from the focus to the dam site (r_1), see Fig. (13). This small difference in the path length travelled by the waves of the tremor would not be able to cause the drop in the energy. The energy drop observed is, however justified for shallow paths (r_2) and (r_2') i.e. the focal distance from the dam site must be many times less than that from the focus to the

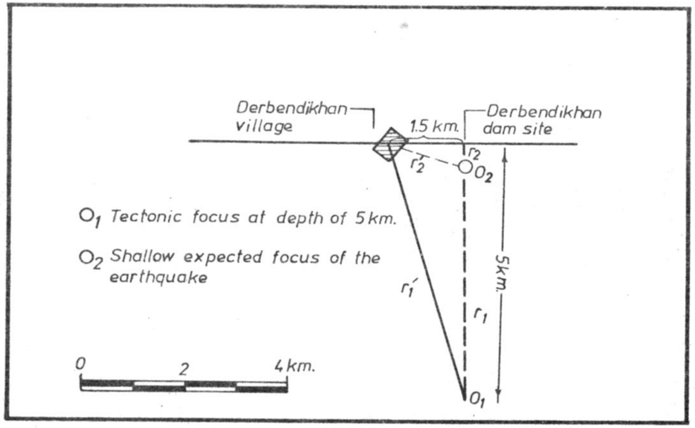

Fig.13. Origin of Derbendikhan 27th Nov.1974 earthquake shock.

site of Derbendikhan village. Hence they are a very shallow focus earthquakes and most likely a reservoir induced shocks than due tectonic movements. This is simply because a very shallow tectonic earthquake due faulting produce enormous amounts of energy of a devastive nature (Faccioli and Rsendiz [26]) much more than what we had experienced during the above discussed shocks.

It is believed also that the three shocks were originated at the dam site, somewhere in the area of the right abutment of the dam for the following reasons :

A. The right abutment is a highly stressed due to the fault intersection , see area (A) of Fig. (6a) and the discussion in section 5.

B. Existence of a hydraulic continuity, see discussion of section 5. Both factors 1 & 2 are favourable engineering conditions for reservoir induced seismicity.

C. That the only right abutment and the right side body of the dam was affected by the three shocks. For instance there was rockfall in the right abutment slopes. Also there was enlargement of the construction joints in the Cantilever portion of the spillway on the upstream side (5-6 mm at the time of the earthquake), opening of the pipe fencing (8-10 mm), minor cracking and spalling of concrete in this portion. Horizontal cracks were observed in the vertical wall of crane gallery, El-Yussif and Jindal [48].

Recent seismicity investigation of Derbendikhan area carried out by Ayar [49] using portable three component high gain short period seismographs have proved induced seismicity at Derbendikhan reservoir.

(8) DISCUSSION AND CONCLUSIONS

The thorough evaluation of the seismo-engineering geological conditions of Dokan and Derbendikhan dam sites and reservoirs has lead to the following main conclusions :

1. Derbendikhan dam is situated in a relatively unfavourable engineering site because of the faulting condition and the sliding problem.
2. Derbendikhan dam type as a rockfill suit much the site condition than concrete type of dam for the following reasons :-
    - A. The hetrogeneous and relatively low strength shale member of the Buff formation foundation rock bear well rockfill dam than concrete type of dam.
    - B. Due to the frequent natural and induced reservoir seismicity in the area, the well designed and constructed rockfill dam of Derbendikhan, although dislocate more than concrete dam by shock waves, but generally have the capacity to adjust to minor displacements without failure.

C. In the Earthquake region of Derbendikhan dam site with faults the possibility of fault movement exists, no matter what the likelihood may be extremely small. At such site if fault or the extension of the foundation fault displaces, the dam sections on opposite sides will be offset by the same general amount and direction as the fault displacement for a rock-fill dam, the main potential hazard is from a concentrated leak developing suddenly along the rupture surface formed in the dam. The hazard can be eliminated by provision of a dequate interval zoning to control the leakage safely. For concrete dam, a fault movement can break the contact between the dam and the foundation, allowing full uplift pressure to act underneath, reducing the shearing resistance along the base and causing failure by sliding on the foundation of the general type which resulted in the disaster at Francis dam in the southern california in 1928, Whlstram [50].

3. Monitoring and stabilization of the rock slide at Derbendikhan dam site - Monitoring and prediction of the slide instability can be made with methods which involve the measurement or detection of displacements on the rocks. Surveying methods provide cheap and reliable means of detecting movements. However, errors associated with these movements must be within acceptable limits. Of the

surveying instruments, the electro-optical devices offer great scope for future investigations, John and Thomas [51] . Seismic techniques have also been found to provide satisfactory results, Wisecarver et al [52] . It is considered, however, that until further developments in the interpretation of the seismic techniques have been achieved, their use, at present, should be confined to comparing the results obtained from displacement measurements. Of the various methods that can be used for stabilising an unstable slope, effective drainage is the primary approach. The use of artificial stabilization techniques such as rock bolts, grouts or retaining walls might be considered as an alternative or complementary to other precautions. Thoughts may also be given to the partial or the complete removal of the unstable rock mass. Economical implications of these alternative courses of action must be considered before any decision on any one or more of these techniques are made.

REFERENCES

1. A. Hassan and M. Mashkour, Mean annual precipitation in Iraq, Journal of the geological society of Iraq, Vol. V, p. 119-129. (1972).

2. INOC document. Geological conditions and hydrocarbon prospects of the Republic of Iraq (Northern and Central parts), INOC document No. 19, INOC Library, Baghdad, (unpublished). (1971).

3. T. Buday. Explanatory notes to the structural sketch map of Iraq : State organization for minerals, library report, (unpublished), 27 p. (1970).

4. Binnie, Deacon and Gourley. Dokan dam project: Directorate General of Dams and Reservoirs, Library report, (unpublished). (1955).

5. Harza Eng. Company. Project planning report of Derbendikhan dam, Vol. I and II. Directorate General of Dams and Reservoirs, library report, (unpublished) (1954).

6. Directorate General of Dams and Reservoirs, technical report. Subcontract for sealing of gorge and strengthening of left bank peninsula - Directorate General of Dams and Reservoirs, library report, (unpublished). (1953).

7. Directorate General of Dams and Reservoirs technical report. Dokan Scheme - documents accompanying tender for the rock sealing contract. Directorate General of Dams and Reservoirs, library report, (unpublished). (1953).

8. Binnie, Deacon and Gourely. Further site investigation for Dokan dam project. Directorate General of Dams and Reservoirs, library report, (unpublished). (1954).

9. R.C.S. Walters. Dam geology. Published by Butherworths publishers and Company, London (1962).

10. S. Abdul Rahman, and S. Al-Immam. Dokan dam. The Engineer Magazine, Oct. p. 15-26. (in arabic). (1962).

11. E. Nonveller, and F. Sabarly. Dokan dam project. Leakages from Dokan dam reservoir. Preliminary report, Directorate General of Dams and Reservoirs, library report, (unpublished). (1973).

12. Bellier Coyneet Derbendikhan dam, final reports of expects on the condition of the dam. Directorate General of Dams and Reservoirs, library report, (unpublished). (1976).

13. Nonveiller and F. Sabarly. High piezometric levels at Derbendikhan dam. Directorate General of Dams and Reservoirs, library report, (unpublished). (1973).

14. Coyne and Bellier. Derbendikhan dam. Analysis of dam behaviour - Review of previous reports recommendations, Directorate General of Dams and Reservoirs, library report, (unpublished), (1955).

15. S. Abdul Rahman, and S. Al-Safi. Report on some technical problems in Dokan and Derbendikhan dams. Directorate General of dams and Reservoirs, library report, (unpublished), (in arabic), (1975).

16. Directorate General of Dams and Reservoirs, special committee report on the site investigation of the sliding area on the right abutment upstream of Derbendikhan dam. Directorate General of Dams and Reservoirs, Library report, (unpublished), (1971).

17. A.R. Jawad, and S.A. Hafez. Geological report on Derbendikhan dam site sliding. Directorate General for dams and reservoirs, Library report, (unpublished). (1972).

18. Directorate General for dams and reservoirs internal committee report on the sliding on the right abutment of the mountain slopes upstream of Derbendikhan dam, Directorate General for dams and reservoirs, library report, 3 P., (unpublished), (in arabic).

19. E. Noda. Water waves generated by landslides, Journal of waterways, Harbors and coastel Eng. Division proceeding of the American Civil Engineers, 96, WW4, p 835-855. (1970).

20. S. Hitchen. Final report on the selection and detailed investigation of a site dam on the Diyala river at Derbendikhan. Directorate General for dams and reservoirs, Library report. (unpublished), (1949).

21. A.A. Nowroozi. Focal mechanism of earthquakes in Persia, Turkey, West Pakistan and Afghanistan and plate tectonics of the middle east. Bulletin of the Seismological Society of America, Vol. 62, No. 3 p 823-850. (1972).

22. S. Al-Sinawi, and H.A.A. Galib. Seismicity and Seismotectonics of Iraq,1975. Bulletin of the College of Science, Vol. 6, No. 2. p. 369-413. (1975).

23. G. D. Louderback, Faults and earthquakes, Bulletin of the seismological society of America, vol. 32, no. 4, p. 305-330, (1942).

24. D.E. Hudson, and R.E. Scott, Faults motions at Baldwin Hills reservoirs, Bulletin of the seismological society of America, vol. 55, no. 1, (1965).

25. N. N. Ambrayses, Studies in historical seismicity and tectonics. Geodynamics today, Roy. Soc. London, vol. 1, p 7-16, (1975).

26. E, Faccioli; and D. Rsendiz, Chapter 4. In the book "seismic risk and engineering decisions" edited by Clomnitz and E. Rosenblueth, Elsevier Scientific publishing Company, N.Y., (1976).

27. C. R. Allen, "Geological criteria for evaluating seismicity in the book "Seismic risk and engineering decisions" edited by Clomnitz and E. Rosenblueth, Elsevier scientific publishing company, N.Y.,(1976).

28. J. L. Sherard, L. S. Cluff and C.R. Allen, Potentially active fault in dam foundations, Goetechnique, vol, 24, no. 3, p 367-428, (1974).

29. G. W. Housner, Intensity of earthquakes ground shacking near the causative fault, proceedings of the third world conference on earthquake engineering New Zealand, (1965).

30. S. Tillotson, The seismology of north eastern Iraq with special reference to the Bekhme-Rowanduz area, in the report "Dokan dam project, vol. I, Directorate General for dams and reservoirs, libarary report (unpublished), (1955).

31. N. I. Nikolaev, Tectonic conditions favourable for causing earthquakes occurring in connection with reservoir filling, Engineering geology, no. 1/2, (Special issue of seismic effects of reservoir impounding), (1974).

32. M. L. Williams, The stresses around a fault or crack in a dissimilar media, Bulletin of the seismological society of America, vol. 49, no. 2, p 199-204, (1959).

33. P. St. Amand, Two proposed measures of seismicity, Bulletin of the seismological society of America, vol. 46, p 41-46, (1956).

34. M. Mashkour, A seismological study in a mining area, Ph.D. Thesis submitted to the University of Strathclyde, 176 p (unpublished), (1976).

35. N. Hast, The state of stresses in the upper part of the earth's crust, Tectonophysics, vol. 8, no. 3, p 113-117, (1969).

36. S. V. Medvedev, Engineering seismology, published by the Academy of Science of the U.S.S.R., Moscow, 1962 (Translated), (1962).

37. H. M. Westergaard, and A. W. Adkin, Deformation of earth surface due to weight of Boulder reservoir, U.S. Bureau of Reclamation, Denever, Colorado, Technical memorandum no. 422, (1934).

38. D. D. Carder, Seismic investigations in the Boulder dam area, 1940-1944 and the influence of reservoir loading on local earthquake activity. Bulletin of the seismological society of America, vol. 35 p 175-192, (1946).

39. J. C. Jaeger and N.G.W. Cook, Fundamentals of Rock Mechanics, Publ. Methuen and Co. LTD. London, (1969).

40. M. D. Evans, Man made earthquakes in Denever, Geotimes, vol. 10., p 11-17, (1966).

41. C. B. Raleigh, Underground waste management and enviromental implications. Bulletin of the America association of petroleum geologist, vol. 18, p 273-274, (1972).

42. J. P. Rothe, Seismic artificials (man-made earthquakes). Tectonophysics, vol. 9, p 215-238, (1970).

43. H. K. Gupta, B. K. Rastogi and H. Narain, Common features of the reservoir associated seismic activities, Bulletin of the seismological society of America, vol. 62, p 481-492, (1972).

44. D. I. Gough, Incremental stress under a two dimentional artificial lake. Canadian journal of earth sciences, vol. 6, p 1067-1075, (1969).

45. D. I. and W. I. Gough, Stress and deflection in the lithosphere near lake kariba, Geophysical journal, vol. 21. p 65-78, (1970).

46. K. G. Harsh and B. K. Rastogi, Dams and Earthquakes, Elsevier Scientific publishing company, (1976).

47. F. S. Al-Immam, S. Al-Rahman and A. Naji, Short report on the 27th Nov. 1974 Derbendikhan earthquake, Directorate General for dams and reservoirs, Library report, (unpublished), (in Arabic), (1975).

48. F. El-Yussif and R. L. Jindal, First report on earthquake studies of Derbendikhan dam. Sulimaniyah University, Department of Civil Engineering, Library report, (Unpublished), (1975).

49. B. S. Ayar, Seismicity investigation of Derbendikhan area, M.Sc. thesis submitted to the University of Baghdad, (Unpublished), (1978).

50. E. E. Wahlstem, Dams, dam foundation and reservoir sites, publ. prentice-Hall, Inc, (1976).

51. C. M. St. John and T. L. Thomas, The N.P.L. Mekometer and its application in more surveying and rock mechanics. Trans. IMM, April, (1970).

52. D. W. Wisecarver, R. H. Merrill and R. M. Stateham, The microseismic technique applied to slope stability. Trans. AIME, vol. 244, N4, Dec., (1969).

Other References

1. M. H. Juma, Derbendikhan reservoir. The Engineer Magazine, no. 8, p 26-30, (in Arabic), (1958).

2. F. Salman and S. Al-Immam, Derbendikhan dam, the Engineer Magazine, no. 19, p 45-49, (in Arabic), (1962).

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SEISMO-ENGINEERING-GEOLOGICAL STUDY AND PROPOSED SEISMIC INSTRUMENTATION OF HIGH DAMS AT SULIMANIYAH GOVERNORATE, N.E.IRAQ

PART (II) SEISMIC INSTRUMENTATION

M. Mashkour[*]

ABSTRACT

In part 1 of this work, Mashkour [1] , it has been concluded that both effective natural and induced earthquakes are common in the Sulimaniyah governorate, where existing dams have been to a certain degree affected by them.

The present part (part 2) deals with the desirability of installing seismic instrument on and near the dams. Recommendation of minimum instrument requirements to cover two types of earthquakes problems are explained: (1) Local seismograph network for determining the local seismicity and (2) Strong motion accelerographs for recording potentially destructive ground shacking and resulting dam vibrations or dam response to earthquake.

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(1) INTRODUCTION

Well detected and accurately located small earthquakes are important for the total seismic evaluation in the area under study. These small earthquakes are oftenly escape from the standard long period seismographs (Tele-seismic network). Therefore it is essential for a local short period seismographs network in the Sulimaniyah governorate to be designed with suitable source/station geometry.

Dokan and Derbendikhan dams were certainly have withstanded a forced horizontal shaking motion, at their foundation when subjected to earthquakes commonly occurs in the vicinity of the structure. The induced vibrations in the structure, where by only results are possible disconfort of inhabitants or more minor damage of secondary elements may occur. However, more than often, the induced earthquakes vibrations in the structure may will take it well into the nonlinear or inelastic range, resulting in permenant damage of the structure. If structural damage has occured, there is no way without the measurements to compare behaviour with design earthquake conditions, to estimate performance for other, perhaps shocks, or to make rational design decisions for repair and strengthening of the structure. If no obvious damage has occured, it is difficult without measurements to decide on the extent to which elaborate and expensive inspection operations should be carried out. Thus it follows the need for suitable recording instruments i.e. strong-motion accelerographs to measure the severity of earthquake ground motion and of the dam response.

(2) SEISMIC INSTRUMENTATION (GENERAL)

The instrument used by seismologists have been carefully designed for the specific research interest of geophysicists. This has resulted in devices that are unsuitable for direct engineering application for the following reasons:

(1) The seismologists desires to record small earthquakes occurring at any point in the earth. This requires sensistive instrument of high magnification. A strong earthquake near the instrument will usually displace the reading off scale or may even damage the instrument. The engineers requires a rugged device that will accurately record the heaviest shocks in the near vicinity of the instrument.

(2) Since a study of the internal constitution of the earth has been a primary objective of seismologist, his instruments are founded if possible on solid conditions. The engineer wishes to know the ground motion at the sites at which engineering structures are located, often on thick alluvium or at locations otherwise quite unsuitable for seismological observations.

(3) For seismological investigations, accurate absolute timing of wave arrival times is essential, whereas the measurement of true ground motion is often of little importance. The engineer does not need absolute time, but true ground motion must be accurately known if the effects of the

Table 1.

Earthquakes designated for Sulimaniyah governorate for the period (1900-1976).

Date			Time			Lat.N	Long.E	Depth (Km.)	Mag. (M)	No. of Stations	Source
Day	Month	Year	Hr.	M.	S.						
11	4	1909	04	02	00	36.0	45.0	-	5.6	-	1 and 2
18	6	1923	-	-	-	34.8	46.0	-	-	-	3
10	5	1930	11	03	00	35.0	46.0	-	4.6	-	1 and 2
10	5	1930	11	07	00	35.0	46.0	-	4.6	-	1
07	5	1932	-	-	-	36.3	44.9	-	4.6	-	1
09	4	1940	-	-	-	35.5	45.6	-	5.5	-	1
25	10	1940	-	-	-	36.8	45.1	-	5.5	-	2
17	2	1944	-	-	-	36.0	45.0	-	5.5	-	2
28	6	1944	02	57	21	36.0	45.0	-	5.5	-	1
02	3	1946	20	46	58	35.3	45.6	-	4.5	-	1
27	7	1946	16	25	43	36.0	46.0	000	5.5	-	4
17	8	1946	09	48	06	35.0	46.0	000	5.5	-	4
17	8	1946	23	37	40	35.0	46.0	000	5.5	-	4
11	2	1948	15	31	16.9	35.52	46.0	-	4.7	-	1
05	5	1958	05	21	37	35.7	44.8	64	5.4	88	4
15	11	1964	06	33	21.5	35.67	45.6	05	4.7	18	4
09	9	1964	22	19	43	35.02	45.96	69	4.5	41	5
12	12	1965	03	31	51	35.1	45.8	-	4.5	-	1 and 2
01	2	1966	07	07	46	35.1	46.0	4	4.4	15	1 and 2

1. Al-Sanawi, S., and Galib, H.A.[2]
2. Al-Jassar, T.,[3]
3. Al-Timimi, F., (1969)[4]
4. Nowrooz, A. A., (1976)[5]
5. Nowroozi, A. A., (1971[6]

earthquakes on structure are to be determined. Thus it will be seen that the fundamentally different objectives of the engineer will require a basically different instrumentation than that needed for seismological studies. It is not implied that the engineer does not derive immense benefits from the activities of the seismologists. It is from the seismologist that the engineer learns of the distribution of seismicity in time and space over the earth and thus can evaluate at any given site the probability of occurrence of earthquakes of various sizes. Therefore there is a need for two types of instrumentations and these are dealt with as follows :

(3) LOCAL SHORT PERIOD SEISMIC NETWORK

Seismic events designated for the area for the period 1900-1976 are Tabled in Table (1). These are usually collected from the bulletin of various international seismological agencies, but they are too few to give adequate indication of real seismicity in the area. For Iraq, the published information is usually limited to certain magnitude. This can be inferred very well from the Fig. (1) for the seismicity of Iraq (1900-1971) after Al-Jassar [3] , in which the slope of a straight line gives the relation between the logarithms of number of earthquakes with their respective magnitude values. Al-Jassar has noticed that the predicted earthquake of 4.5 magnitude is 50, but the ones found in the available published

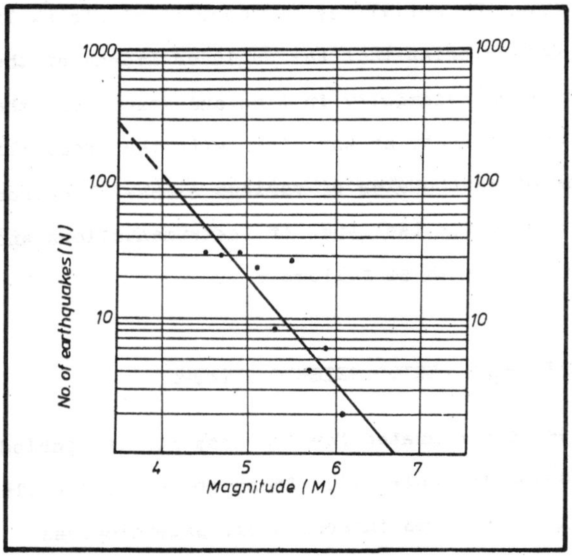

Fig. 1. The relationship between the logarithm of no. of earthquakes with their respective values (After Al-Jassar, 1972)^{3} .

data is 18. Small earthquakes are important for the total seismic evaluation of the area. They help to find any relation between their occurrence and the occurrence of the large earthquake. This is due to the fact that large and small earthquakes probably share the same tectonic causes, and one may learn about the stresses conditions responsible for large earthquakes by studying small but numerous earthquakes.

Small earthquakes with magnitude less than (3) are called micro-earthquakes and they are quite common in the area as indicated by recent seismicity study by Ayar [7] . They usually escape from the world standard long period seismographs (Tele-seismic network stations). Hence the decision to install them in the area will add little to our knowledge of seismicity, since they are not concerned with the observations of near regions small earthquakes. Willmore [8] and Wilmore [9] . Thus for investigation of these small local earthquakes, we require small aperture seismic network with suitable source/station geometry and most important a known velocity structure for the network. These are discussed as follows separately:

3.i <u>Principle design of the short period seismic network.</u>

When shocks occurs in rocks at certain depth, waves travel out radially and in all directions from the disturbance. In solid homogeneous rocks. There are two modes of wave propogation, namely compressional and shear. The compressional, or p- waves travel faster than the shear or S-wave.

If at a point remote from the source, the difference in times of arrival of P- and S-waves can be measured, then the distance from the source to the measuring point can be calculated. For this to be done, the velocities of P- and S-waves must be known. In practice it is not easy to determine when the S-wave arrives because it is usually obscured by the code of the P-wave, especially when P-S interval is short.

Alternatively, if there are two measuring points and the direction of the source is known, the distance of the source can be calculated using the difference in times of arrival of the P-waves at the two measuring points. Consider two seismic stations A,B which record the same surface focus earth tremor epicenter (R) shown in Fig.(2 a). The difference in arrival time at (A) and (B) is (DT). For a single-layer model, Fig. (2 b), in which travel-time is proportional to distance, the locus of constant (DT) is a hyperbola lying between the y-axis (Locus of DT = 0) and the X-axis (Locus of DT = maximum). Any point (R) may be found by specifying some distance (AR) and finding the appropriate distance (BR) for a fixed (DT) from the travel-time curve. A family of such curves are plotted for a pair of stations in Fig. (3) using the assumed travel-time curve in Fig. (2 b). The curves are for equal increments in (DT) of 0.05 sec. The spacing between the hyperbolae is a measure

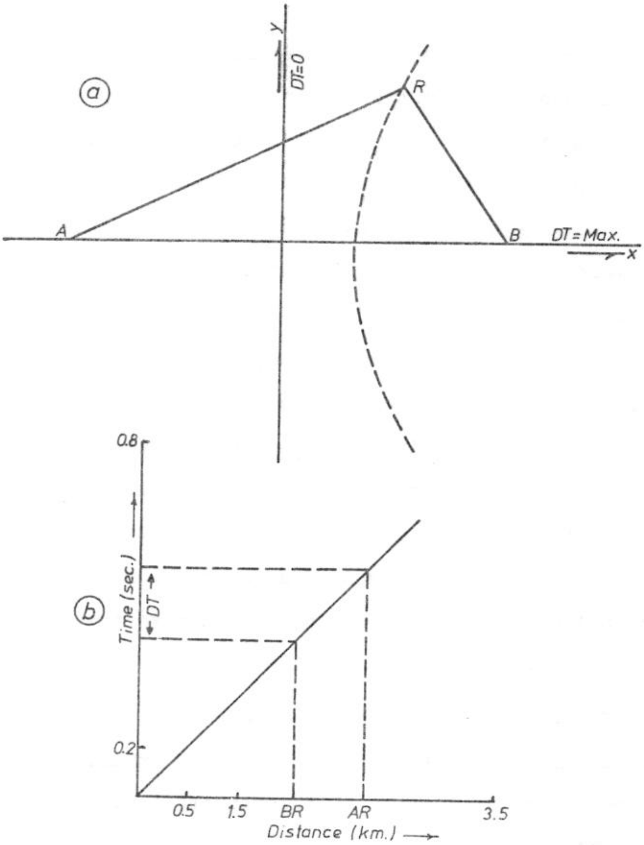

Fig. 2-a. Principle method of epicenter location chart.

Fig. 2-b. Time-distance curve for a single layer.

of the accuracy with which a source point can be located. Imagine a source point which can lie anywhere along a radial line from (O) and making an angle (Q) with the line AB. Along the line Q = 0, between (A) and (B) the hyperbolae are normal to the radial line and are closely spaced, the resolution is best here. Outside (A) and (B) the line is coincident with hyperbola for DT = maximum, and the resolution is zero. The radial line is coincident with the hyperbolae T=0 when Q = 90° and the resolution is again zero. In general, the resolution is best at small angles and close to the origin. From Fig. (3), it can be seen that three measuring points are required to obtain a unique location in two-dimensional space, and that for good resolution, the three measuring points should lie at the corners of an equilateral traingle which encloses the source. Similarly in three dimensions, four measuring points are required to provide a unique solution and the optimum configuration of the four points is at the measuring points surrounding the source will greatly improve the accuracy of the location.

The principle method of seismic network design described above is used for designing the proposed seismic network in the area. The final shape of the network is given in Fig. (4). This network will also enclose many proposed dams projects as shown the figure.

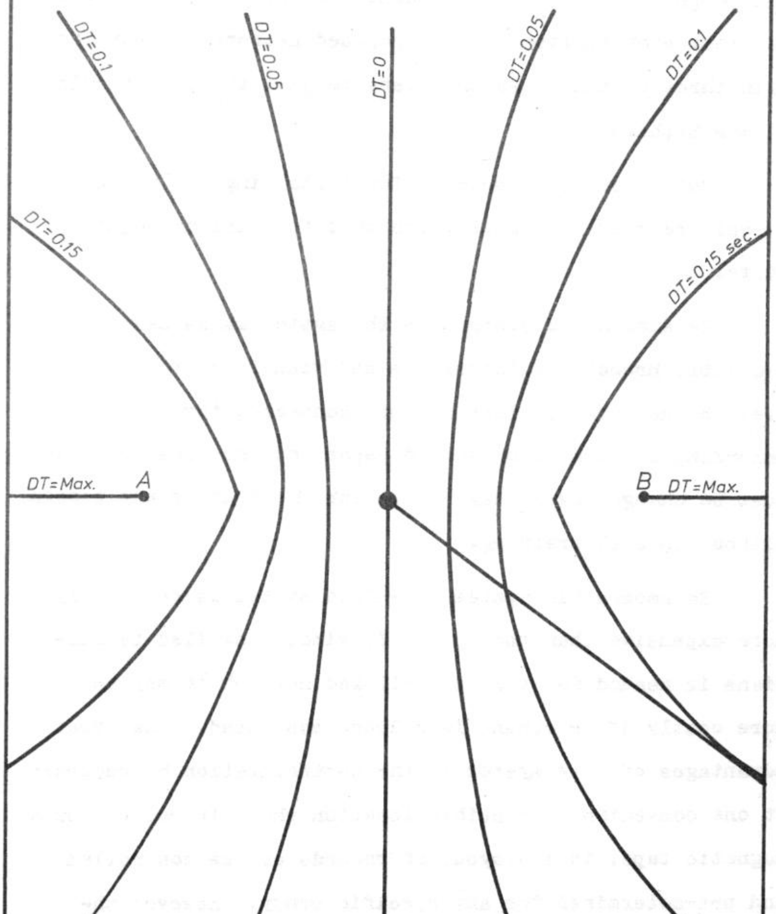

Fig. 3. A family of hyperbolae corresponding to the difference in arrival time (DT) at the seismic stations A & B.

Normally the combination of P- and S-waves gives most information about depth and origin time, but S-waves can be very seldom read sufficiently well especially on the vertical component of the seismograph. Therefore it is recommended that each station of the proposed network be supplied with three component seismometers to give the good reading of the S-phase.

Two alternative schemes for installing the proposed seismic network. Both of which meet the minimum requirements.

Seismographic system I - The system makes use of available probable seismometers and visual recording units i.e. the network stations are not connected together. Recording is usually on smoked paper and the paper records must be changed every day. This can be done by any person without special training.

Seismographic System II - This system is relatively more expensive than the system I, since a skilled technicians is needed for the radio-linked network or may be more costly if telephone land lines was used. The great advantages of this system is the centralization of recording at one convenient accessible location where it records on a magnetic tape, thus playout of records can be controlled and pre-determined for any specific study. However the choice of either separate stations or centrally linked by

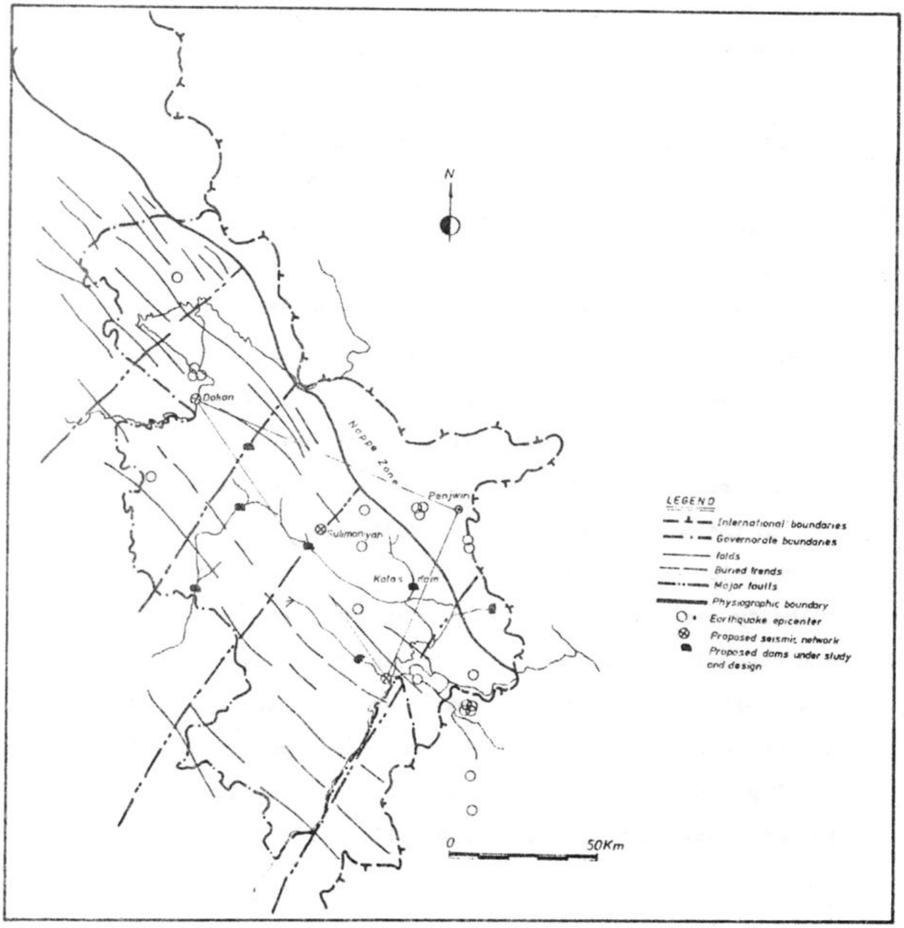

Fig. 4. Proposed seismic network of Sulimaniyah governorate.

telephone wires or radio linked need, further feasibility study should the proposed seismic network is taken seriously in the future, Mashkour [10] .

3.11 Determination of the velocity structure for the seismic network. The lithological changes of this part of geosynclinal resulted in subdivision of the crust sedimentary cover as shown in Fig. (5). Such changes has resulted in the velocity changes and hence gave major prominent seismic reflectors. These are usually determined by conducting deep seismic soundings along few profiles with an area of a few tens of km's. from the reservoir. This is a rather expensive proposition and has not been conducted yet in the area under study. An alternative preliminary calculation of velocity-structure is made by studying the velocity measurements across different types of cenozoic and mesozoic age already measured in different kirkuk and Mosul oil wells, (personal comm.) and from the major lithological changes in the stratigraphic section, INOC [11] and Fig. (5). The final estimate of the velocity - structure for the network is given in Table (2) below :

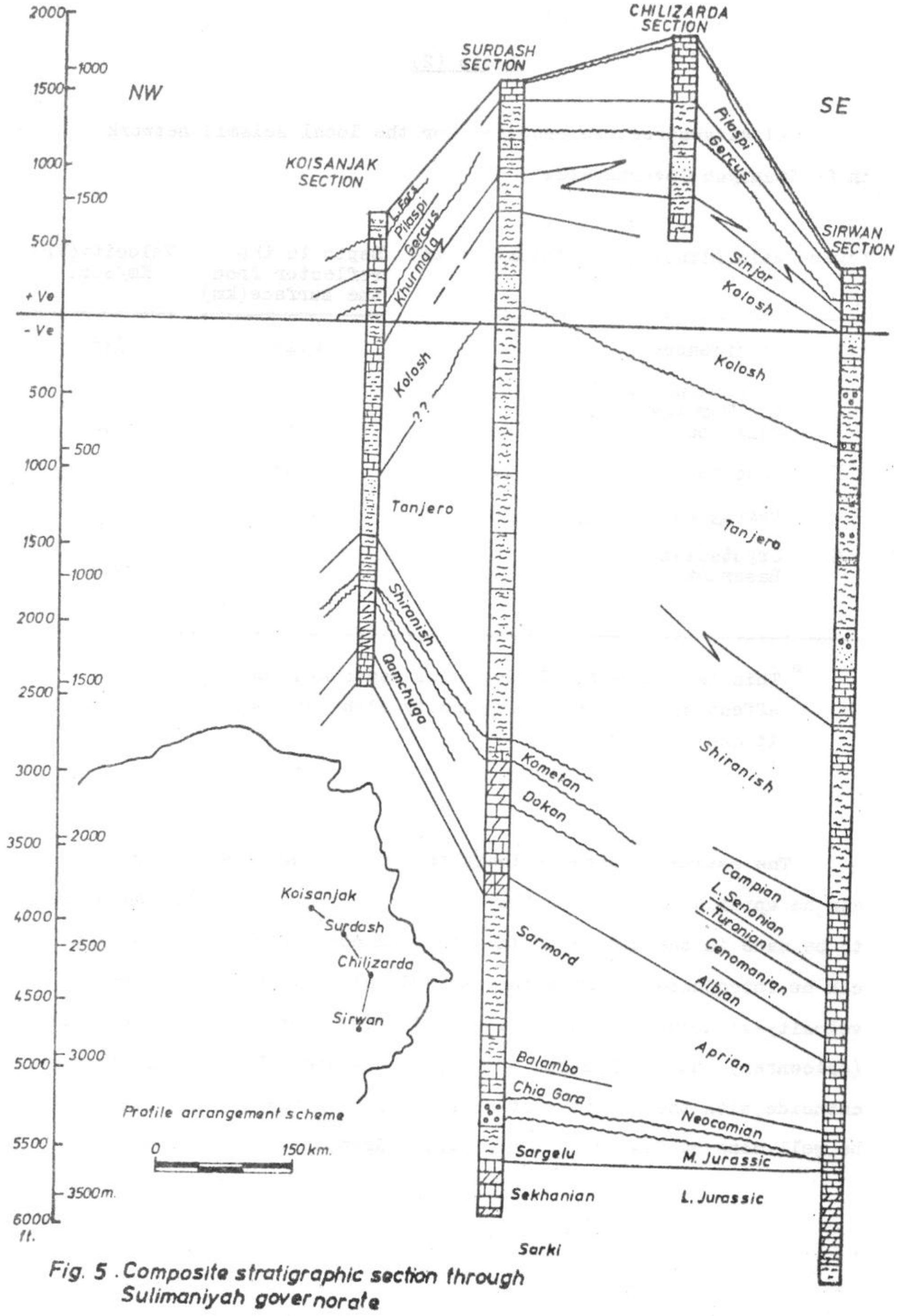

Fig. 5 . Composite stratigraphic section through Sulimaniyah governorate

Table (2)

Velocity-structure proposed for the local seismic network in Sulimaniyah Governorate.

Layer	Main Lithology	Thickness(km)	Depth to the reflector from the surface(km)	Velocity(VP) Km/Sec.
1	Terrigenous	0.15*	0.15	3.5
2	Calcureous (Top) and Terrigenous Calcareous (Bottom)	2.5	2.65	4.42
3	Calcareous	2.0	4.65	5.3
4	Terrigenous	3.0	7.65	6.3
5	Crystalline Basement.	-	-	8.1

* This is a very small thickness layer and has little effect on the proposed velocity structure model. Hence it can be neglected.

The estimated three velocities for the three layer structure can be applied to find the locus of one or two big artificial shots to be made in the middle of the proposed network and modification can be introduced to the thickness and velocity of the assumed velocity-structure given in Table (2) above, until the map position (epicenter) and focal depth of these shots are well approximately coincide with the actual surface and depth of the shots. This can be well done by fast computer program, Crampin and Willmore [12]

(4) STRONG MOTION ACCELEROGRAPHS

Completely adequate definition of input ground motions and dam response would require a large number of accelerographs at carefully selected points. For major dam projects, in highly seismic regions, detailed studies of the optimum number and location of accelerographs would be expected for the special conditions of the particular site. For minimum recommendations, however, equations of location are secondary to the prime object of ensuring that at least some information of engineering value will be obtained for all strong shaking. For this purpose, it is recommended that not less than four strong-motion accelerographs be installed. Two of these should be located to record earthquake motions in the foundation and two to measure dam response, Bolt and Hudson [13]. The foundation instruments can often be mounted to dam abutments, or at an appropriate site in the immediate vicinity of the dam that is not obviously influenced in a major way by local geologic structural features. The instruments to measure dam response can usually be mounted at two different locations on the crest or in upper galleries should they exist, avoiding special superstructures which may introduce localized dynamic behaviour.

When strong earthquake occurs near an instrumented dam, the accelerographs records will be studied and if the recorded acceleration exceeds 15 % g __ M = 5.5, then there is evidence of overstressing of the dams, then it would be advisable to make a special study of the implications of the recorded accelerations as regards stresses and strains developed in the dam during the earthquake, see Bolt and Hudson [13].

By simultaneous measurements of ground motion and structural response during actual earthquakes, a great deal of information on the dynamic characteristics of structure under earthquakes excitation can be derived, and this will be of great value, when other dams are to be constructed in the North and North Eastern region of Iraq.

(5) CONCLUSIONS

I. Most of the earthquakes originated in the area under study were recorded by the low density long period seismic network in the neighbouring countries. In order to examine the seismic phenomena more closely, a high density short period seismic network was suggested. So that every small magnitude seismic shocks which otherwise escaped recording by the world long period seismic stations but are important for the total evaluation of the seismic activity could be recorded.

II. To study either earthquakes damage or reservoir induced seismicity, it is essential that a network of seismographs adequate for approximate location of small local earthquakes must be in operation before the impounding of the reservoir, without such a network it is usually impossible to establish the seismicity of the area prior to closure. Thus the extent to which local earthquakes where a consequence of the reservoir, or were part of a more general seismic pattern, can not be decided. Such a decision is essential to an evaluation of the probable size and location of future shocks and thus is of immediate practical importance. It might be of great interest to start such projects with under constructions in difrerent parts of Iraq.

III. For velocity-structure determination for any network, on alternative cheap proposition of determination is suggested. This is by locating seismic station at certain interval along a certain profile and will records accurately timed explosions used for the excavation and earthworks at the dam site. Time distance curve can be constructed from which the velocity-structure can then be calculated.

ACKNOWLEDGMENT

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REFERENCES

1. M. Mashkour. Seismo-Engineering-Geological study and proposed seismic instrumentation of high dams at Sulimaniyah governorate - Part 1. Seismo-Engineering geological study. Al-Mustansiriyah Journal of Science, 197, vol. pp. 1978.

2. S. Al-Sinawi, and H.A.A. Ghalib. Seismicity and seismotectonics of Iraq, Bulletin of the College of Science, Vol.6, No.2, 1975, p, 369-413.

3. T.J. Al-Jassar. Seismicity of Iraq (1900 - 1971), General Directorate of Mineral Exploration and Prospecting, Library report No. 639, p. 43-64. 1972.

4. F.S. Al-Tamimi. Seismicity of Iraq, Journal of the Geological Society of Iraq, Vol. 2, No. 1, p. 32-47. 1969.

5. A.A. Nowroozi. Seismotectonics provinces of Iran, Bulletin of the Seismological Society of American, Vol. 66, No. 4, p. 1249-1276. 1976.

6. A.A. Nowroozi. Seismo-tectonic of the Persia Plateau, Eastern Turkey, Cancasus, and Hindukush Regions, Bulletin of the Seismological Society of America, Vol.61, No.2, p. 317-341. 1971.

7. B.S. Ayar. Seismicity Investigation of Derbendikhan area, M.Sc. thesis submitted to the University of Baghdad (Unpublished), 1978.

8. P.L. Willimore. New Methods in Seismology, Quarterly Journal of the Royal Astronomical Society of London, Vol.14, No. 4, p. 391-405 1963.

9. P.L. Willimore. A Strategy for Seismology. Geophysical Journal of the Royal Astronomical Society of London, Vol. 8, No.2. p. 242-248. 1963.

10. M. Mashkour. A Study about the Possibility of Establishing a National Seismic Network in Iraq, submitted to the Earthquake Center of the Foundation of Scientific Research, Baghdad, 12 p. (in arabic), 1977.

11. INOC document. Geological Conditions and Hydrocarbons Prospects of the Republic of Iraq (Northern and Central Parts), INOC Document No. 19, INOC Library, Baghdad (unpublished). 1971.

12. S. Crampin, and P.L. Willmore. Small Earthquakes Observed with Local Seismometer Networks. Philiosphical Transaction of the Royal Society of London, A 274, p. 383-387. 1973.

13. B.A. Bolt, and D.E. Hudson. Seismic Instrumentation of Dams. Journal of the Geotechnical Engineering Division, American Society of Civil Engineers, Vol. 101, No. GT 11, proc. paper 11697, p. 1095-1104. 1975.

OTHER REFERENCES

1. **J. Solnes. (edi.). Engineering Seismology and Earthquake Engineering, Publ., Noordhoff-Leiden. 1974.**

2. **C.F. Richter. Elementary Seismology, Publ. W. H. Freeman. 1958.**

3. **N.M. Newmark, and E. Rosenblueth. Fundamentals of Earthquake Engineering. Publ. Prentice-Hall, INC. 1971.**

THE RATE OF CHANGE OF MOLECULES DISORDER IN WATER FROM 273.1^{o}K UP TO 343.1^{o}K

Tariq Al-Dhahir* and Abdul-Sattar Al-Ani*

ABSTRACT

Using previous experimental data[4,5], the two parts of the variation of the relaxation wavelengths descrease as temperatures increase.

Taking the values of $\delta\lambda_{s_2}$, the rate of change of the molecules disorder was found. It was calculated that, as the rate of change of the molecules disorder decreases; the percentage of the bonds broken increases.

INTRODUCTION

Dielectric properties express the response of a system to an electric field; response which is charactarized by a variable macroscopic polarization [1]

Since H_2O is a polar molecule; it has 4-bonded, 3-bonded, 2-bonded, 1-bonded and zero bonded molecules. The order of the system is changing with rising temperatures while the electric field is fixed at a certain frequency.

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THEORY

According to the theory of rate processes, [2] the relaxation time of the polar substance is given by:

$$\tau = \frac{h}{KT} e^{H/RT - S/R} \qquad \ldots\ldots\ldots\ldots \qquad (1)$$

where (H) is the activation energy

(S) is the entropy

(h), (K), (R) and (T) have their usual significance.

We have [3] $\lambda_s = 2\pi C\tau$ .... (2)

where (C) is the light velocity.

(τ) is the time spend by the molecule near one of its equilibrium position before jumping to the other equilibrium position.

(λ_s) is the wavelength which corresponding the frequency (the so-called "Sprungwellenlage")

Combined equation (1) and (2), then differentiate the result with respect to temperature; after assuming the variation of (H) with respect to temperature is very small and can be neglected;

$$\frac{d\lambda_s}{dT} = - \lambda_s \left[\frac{H}{RT^2} + \frac{1}{T} + \frac{1}{R} \frac{dS}{dT} \right] \ldots\ldots \qquad (3)$$

For small intervals of temperature we can write:

$$\delta\lambda_s = -\lambda_s \left[\frac{H}{RT^2} + \frac{1}{T} + \frac{1}{R} \frac{dS}{dT} \right] \delta T \ldots\ldots \qquad (4)$$

When $\delta\lambda_s$ is the decrease in the relaxation wavelength when the temperature is rising an interval δT.

Choosing:

$$\delta\lambda_{s1} = -\lambda_s\left[\frac{H}{RT^2} + \frac{1}{T}\right]\delta T \quad \ldots\ldots\ldots \quad (5)$$

and

$$\delta\lambda_{s2} = -\lambda_s\left[\frac{1}{R}\,\frac{dS}{dT}\right]\delta T \quad \ldots\ldots\ldots \quad (6)$$

$$\delta\lambda_s = \delta\lambda_{s1} + \delta\lambda_{s2} \quad \ldots\ldots\ldots \quad (7)$$

Since $\delta\lambda_s$ is the decrease in the relaxation wavelength due to increase of temperature. $\delta\lambda_{s1}$ is the decrease in the relaxation wavelength due to thermal agitation. $\delta\lambda_{s2}$ is the decrease in the relaxation due to the increase of molecules disorder.

RESULTS AND DISCUSSIONS

According to the experimental data [4,5] the variation of relaxation wavelength ($\delta\lambda_s$) is due to the change of temperature given by:

$$\delta\lambda_s = \lambda_s \text{ at } 10\ n^{o}C - \lambda_s \text{ at } (n-1)\ 10^{o}C$$

Where (n) is an integar number 1, 2, 3, 4, 5 and 6.

The experimental values of relaxation wavelength with temperature as shown in Table (1). Using H = 2.5 kcal/mole 6 ; equation (5) and (7); the values of $\delta\lambda_{s1}$ and $\delta\lambda_{s2}$ were obtained for different temperatures see Table (2) & Figure (1). From equation (5) $\delta\lambda_{s_1}$ should be negative since (δT) is positive, and $\delta\lambda_{s_2}$ has a negative value too. So $\delta\lambda_{s_2}$ decreases as temperature increases see Figure (1). $\delta\lambda_{s_1}$ and $\delta\lambda_{s_2}$ are never intersected with temperature axis and asymptote at high temperature.

Table (1)
Experimental values of relaxation
wavelength (λ_s) for H_2O

Temperature °K	$\lambda_{s\mathrm{cm}}$
273.1	3.34
283.1	2.43
293.1	1.78
303.1	1.36
313.1	1.1
323.1	0.91
333.1	0.76
343.1	0.65

Table (2)
Variations of the relaxation
wavelengths with temperature

Temperature °K	$\delta\lambda_{s\mathrm{cm}}$	$\delta\lambda_{s1\mathrm{cm}}$	$\delta\lambda_{s2\mathrm{cm}}$
273.1	---	---	---
283.1	-0.91	-0.642	-0.268
293.1	-0.65	-0.438	-0.212
303.1	-0.42	-0.303	-0.117
313.1	-0.26	-0.217	-0.043
323.1	-0.19	-0.167	-0.023
333.1	-0.15	-0.13	-0.02
343.1	-0.11	-0.103	-0.007

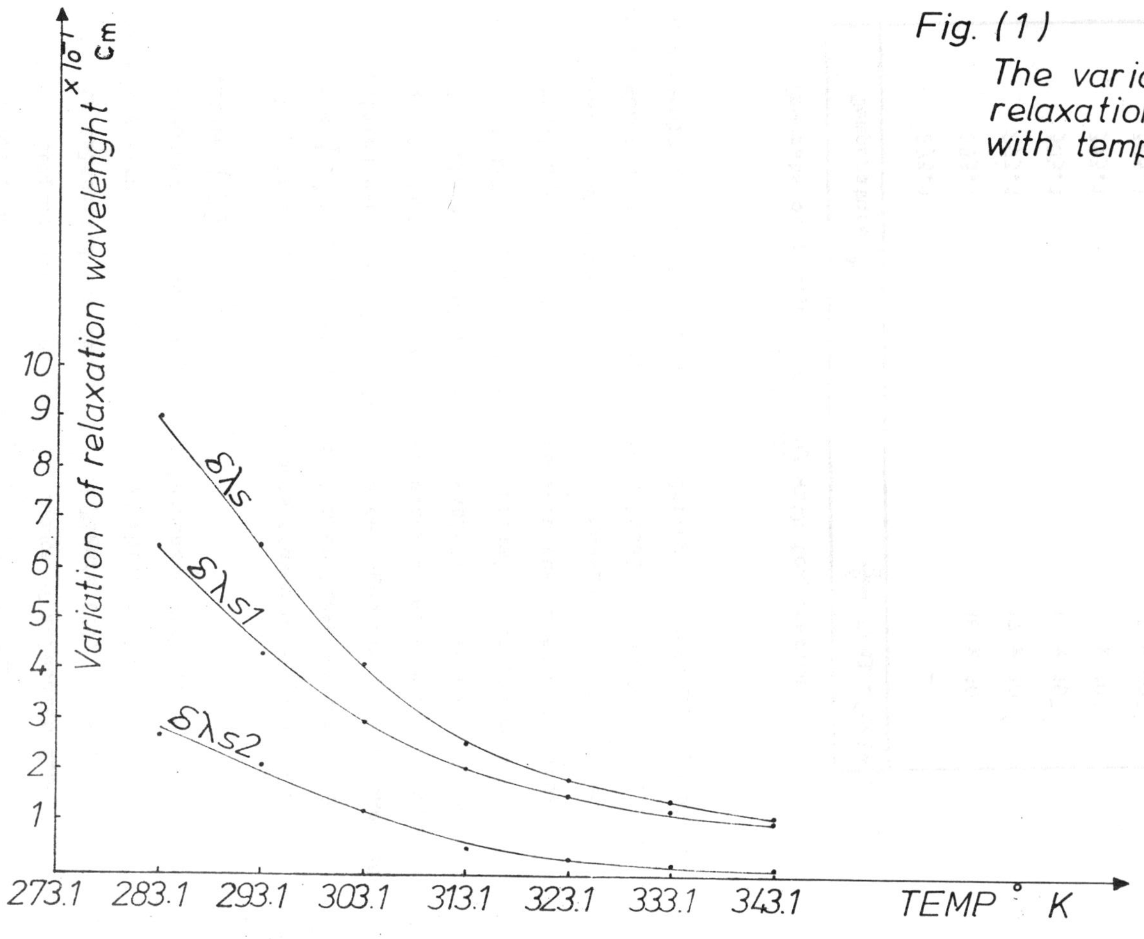

Fig. (1)

The variations of the relaxation wavelenghts with temperature .

By applying the results of $\delta\lambda_{s_2}$ into equation (6) for different temperatures, the rate of change of molecules disorder is calculated see Table (3) and Figure (2). This rate decreases with increasing temperatures while the disorder of the arrangements system as a whole increases with increasing temperature [7].

The percentage (P%) of the bonds broken were taken from references [5] & [6] for the same temperatures as above, which is tabulated see Table (4). These percentages are plotted against the rate of change of the molecules disorder as shown in Figure (3). The obtained results were not satisfied Poisson's distribution and Chi - square. Surface programming was suggested which might give a good relation between the three-dimensional problems. From Figure (3), as the percentage of bonds broken increases the rate of change of the molecules disorder decreases. This result due to the bonds broken during increasing temperature.

Table (3)
The rate of change of entropy with temperature

Temperature ^{o}K	$\frac{ds}{dT}$ Kcal/K^{2}mole
273.1	-
283.1	16×10^{-3}
293.1	17×10^{-3}
303.1	13×10^{-3}
313.1	7×10^{-3}
323.1	5×10^{-3}
333.1	4×10^{-3}
343.1	3×10^{-3}

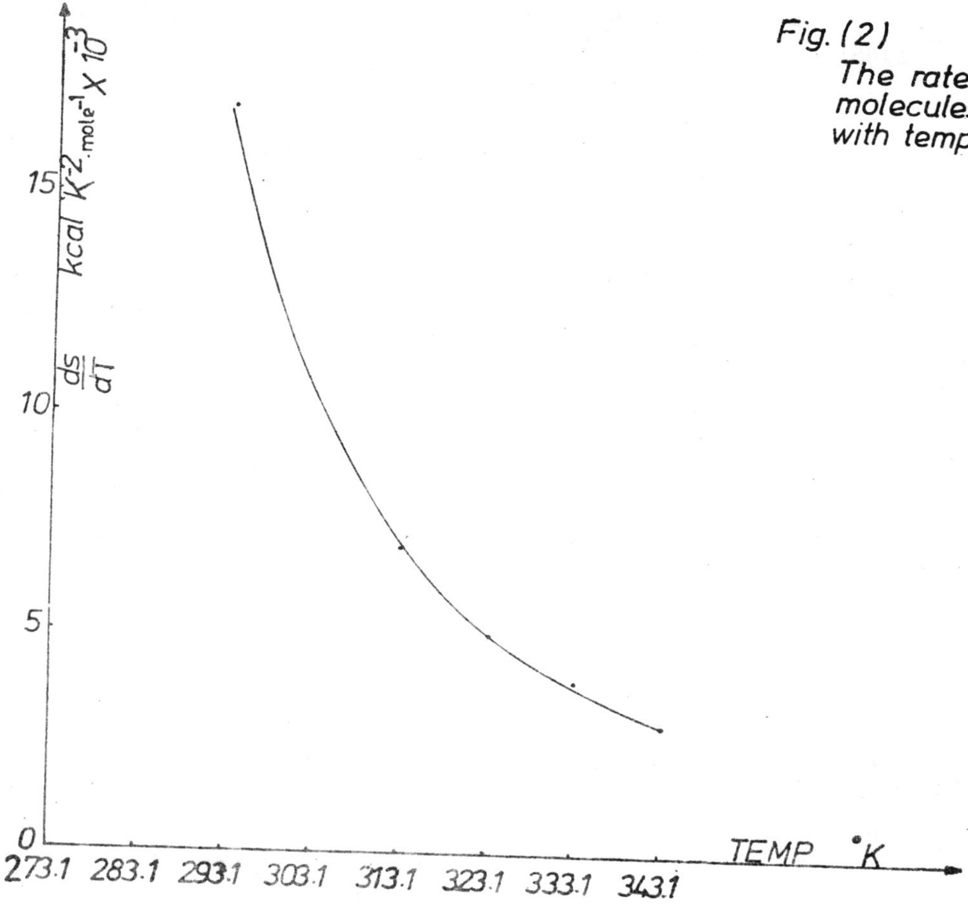

Fig. (2)
The rate of change of molecules disorder with temperature.

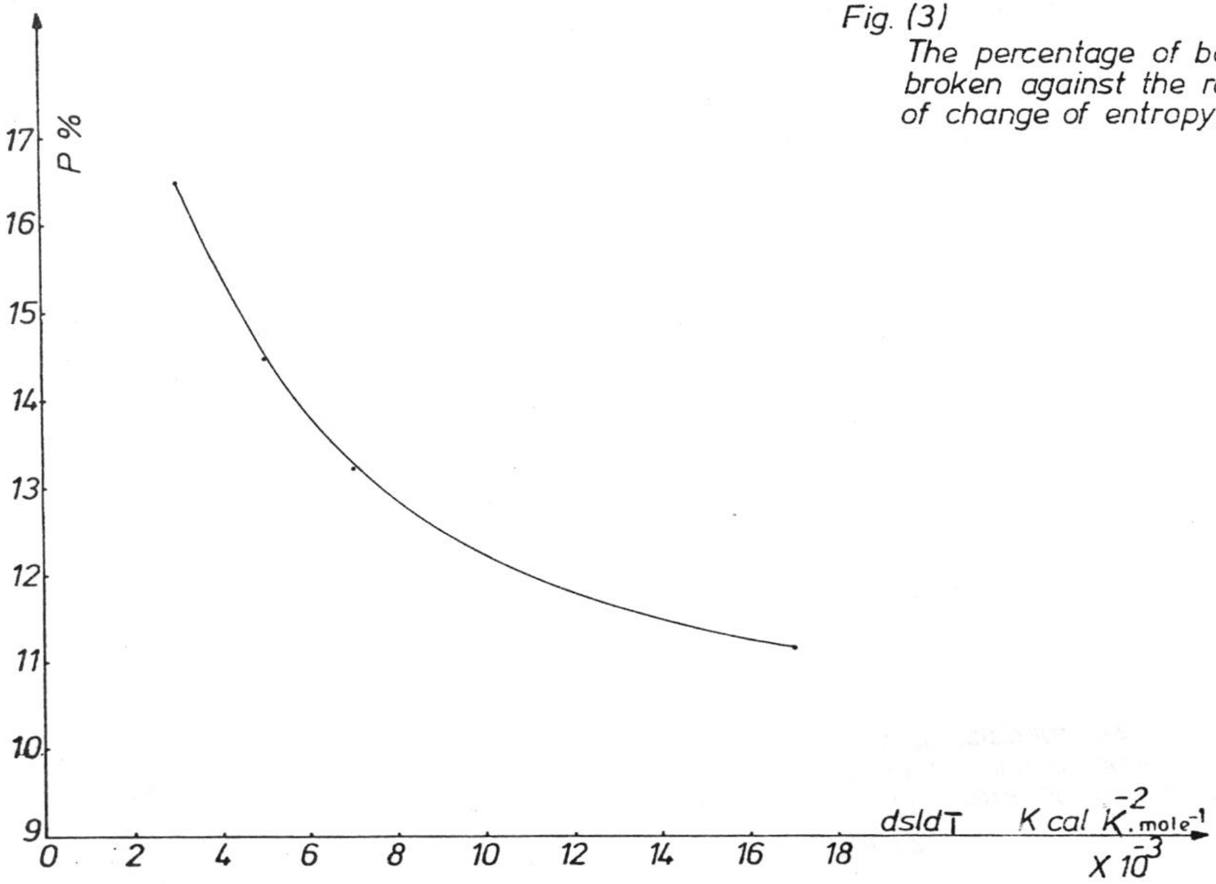

Fig. (3)
The percentage of bonds broken against the rate of change of entropy.

Table (4)

The Percentage of bonds broken with temperature

Temperature ^{o}K	P%
283.1	10
293.1	11.2
303.1	12.2
313.1	13.2
323.1	14.5
333.1	15.7
343.1	16.5

REFERENCES

(1) (a) E. Whalley, S.J. Jones and L.W. Gold, eds.: Physics and Chemistry of Ice. The Royal Society of Canads, Ottawa (1973).

(b) R.A. Horns, ed.: Water and Aqueous Solutions. J. Wiley, New York (1972).

(c) D. Eisenberg and W. Kauzmann: The structure and properties of water, Clarendon Press, Oxford (1969).

(2) H. Eyring, S. Glasstone and K.J. Laidlen; The Theory of Rate Processes.

(3) P. Debye, Polar molecules; chemical catalogue, New York (1929).

(4) G.H. Haggis, et al, The J. Chem. Phys. 20, 1452, (1952).

(5) G.H. Hasted, and Trans. Fara. Soci. 49, 1003, (1953).

(6) T.A. Al-Dhahir: M.Sc. Thesis (1978).

(7) N.E. Dorsey. Properties of ordinary water substances; Hafner New York (1968).

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DECAY SCHEME STUDIES IN ^{152}Gd

B.A. Bishara[*], M.A. Al-Jeboori[*], and K.F. Kaddoumi[*]

ABSTRACT

The decay of 12.4y ^{152}Eu to ^{152}Gd has been studied in a high resolution singles measurement and a Ge(Li) - Ge(Li) coincidence study. The results revealed the existence of 33 gamma-rays in the decay of ^{152}Gd. The ccincidence measurements confirmed thirteen excited states in the decay scheme of ^{152}Gd. The levels at 1283.0, 1319.0, and 1692.2 keV are now confirmed on the basis of coincidence data. A qualitative analysis of the level structure of ^{152}Gd seems to show that this nucleus displays a more rotational nature than a spherical one as previously suggested.

INTRODUCTION

Considerable attention has been given to the characteristics of low-lying levels of the "transitional nuclei" which lie between the spherical ($N \leqslant 88$) and the deformed ($N \geqq 90$) nuclei. The ^{152}Gd with 88 neutrons has been characterised as nearly

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spherical in shape, partially on the basis of vibrational-like spectrum, but this idea has been challenged lately. A revision of the low-lying levels in ^{152}Gd and a study of their properties and their mutual interactions would help in studying the characteristics of transitional nuclei. In this respect, the study of the radioactive decay of ^{152}Eu is very ideal because it populates the levels of ^{152} Gd by negaton decay.

The decay scheme of ^{152}Gd has been the subject of several studies such as the inelastic scattering of deuterons [1] and the radioactive decay of ^{152}Tb [2] and the ^{152}Eu^{m,g} [3] isomeric pair. The different investigations of the ^{152} Eu^{m,g} [4 - 6] have revealed some newly reported levels and some very weak transitions, although the reported results show few differences. In this study, a high energy resolution and high efficiency Ge(Li) spectrometer is used, in singles and coincidence techniques, to study the gamma-ray transitions in ^{152}Gd in order to confirm the gamma transitions between the different states and to study the nature of the different bands.

EXPERIMENTAL PROCEDURE

A point source of ^{152}Eu^{g} of activity approximately equal to ten microcuries is obtained from a commercial supplier [7]. Two large volume (102.8 c.c.) Ge(Li) detectors and a complex gamma-ray spectrometer are used to study the singles and coincidence spectra. A complete description of the equipments used in this study together with the methods of analysis have been given in a previous paper (see reference No. [7] which will be denoted as paper I).

RESULTS

A. Gamma Singles Spectrum

The gamma-ray singles spectrum of the decay of $^{152}Eu^{g}$ is measured by the Ge(Li) single-channel spectrometer shown in paper I. The details of the singles spectrum are shown in the Figures 2 to 5 of paper I, which include all the lines in the decays of both ^{152}Sm and ^{152}Gd. The energies of these lines are determined by the method described before [7] and the errors in calibration are estimated in the same way. Table 1 gives the gamma-ray transitions in the decay of ^{152}Gd as compared with the data of other authors [4 - 6] .

B. Intensity Determination

The relative gamma-ray intensities are determined by summing the counts under each peak by the method of paper I. Table 2 summerizes the results obtained for the relative intensities of the gamma-rays of ^{152}Gd, where all the intensities are given relative to the intense 344.5 keV lines which is considered to have an intensity equal to 100.

C. Coincidence Spectra

The singles spectrum of ^{152}Eu includes all the transitions in both ^{152}Sm and ^{152}Gd decays, the coincidence measurements are carried out to separate the lines belonging to the decay of ^{152}Gd from other lines. The Ge(Li) - Ge(Li) coincidence

Table 1. Energies of gamma rays (in keV) emitted in the decay of ^{152}Gd

Present Study	Riedinger (ref.4)	Varnell (ref.5)	Baker (ref.6)
			209.2
271.1	271.1	271.0	271.03
314.0	315.1		315.18
325.1	325.0		324.9
344.5	344.22	344.2	344.3
352.0			352.0
367.8	367.7	367.6	367.73
		400.5	
410.9	411.11	410.9	411.09
493.6			493.7
			496.4
503.2	503.5	503.3	503.37
511.2	511.3		
519.6	520.2		520.22
			527.3
533.9	534.2		534.3
585.9	586.3	586.0	586.22
	674.7		675.0
678.4	678.6	678.6	678.61
			703.6
			712.0
713.2	713.4	712.9	712.7
764.8	765.0		764.92
779.0	778.81	779.1	778.9
795.0	794.6		794.7

Present Study	Riedinger (ref.4)	Varnell (ref.5)	Baker (ref.6)
931.0	930.7	930.8	930.76
937.2			936.6
974.5			974.4
991.0	989.8		990.05
1089.9	1089.9	1090.0	1089.82
			1109.2
1122.5	1122.9		
1206.0*			1206.1
1233.9	1233.5		
1261.3	1260.9		1261.24
1299.3	1298.9	1299.2	1299.19
1347.6	1347.9		1347.9
1434.2	1433.7		
1448.0	1447.3		
1538.4	1537.4		1538.2
	1606.0		1605.62
1643.6	1643.4		

Table 2. **Energies and relative intensities of gamma rays emitted in the decay of ^{152}Gd.**

Energy (keV)	Relative Intensity
271.1	0.30 ± 0.034
314.0	0.146 ± 0.032
325.1	0.217 ± 0.029
344.5	100
352.0	0.062 ± 0.016
367.8	3.21 ± 0.200
410.9	7.965 ± 0.400
493.6	0.16 ± 0.032
503.2	0.503 ± 0.020
511.2	0.255 ± 0.090
519.6	0.177 ± 0.030
533.9	0.114 ± 0.060
585.9	1.624 ± 0.230
678.4	1.820 ± 0.110
713.2	0.173 ± 0.040
764.8	0.710 ± 0.130
779.0	47.010 ± 0.180
795.0	0.143 ± 0.040
931.0	0.280 ± 0.025
937.2	< 0.01
974.5	0.038 ± 0.011
991.0	0.017 ± 0.020
1089.9	6.201 ± 0.410
1122.5	0.050 ± 0.030

Table 2. (continued)

Energy (keV)	Relative Intensity
1206.0	< 0.04
1233.9	0.101 ± 0.010
1261.3	0.140 ± 0.200
1299.3	5.230 ± 0.180
1347.6	0.061 ± 0.007
1434.2	0.018 ± 0.005
1448.0	0.171 ± 0.011
1538.4	< 0.01
1643.6	0.021 ± 0.002

spectrometer described in paper I has been employed in this study. Five gates set on transitions in ^{152}Gd, are analysed to verify the placements of the gamma transitions in the decay scheme. The gates used are taken at 271.1, 344.5, 410.9, 585.9 and 779 keV; and Table 3 gives a list of the coincidence relationships obtained from these gates. The coincidence spectra gated by the 344.5 and 410.9 keV lines are shown in Figs. 1 and 2 to illustrate some of the results obtained from the coincidence work. Figure 1 shows that the 1206 keV gamma transition which is not seen in the singles spectrum is detected in the coincidence spectrum of the 344.5 keV gate, this transition is estimated to have relative intensity less than 0.05.

The results of the singles and coincidence measurements are shown in the decay scheme of ^{152}Gd (Fig. 3). All the energy states shown in the figure are confirmed in the present study, the transitions indicated by dashed lines in the figure are still doubtful since they could not be observed in the present work.

DISCUSSION

The ^{152}Gd nucleus lies at the edge of the so-called "transitional region" where the level properties of the nuclei having $N \leq 88$ seem to be drastically different from those of the nuclei having $N \geq 90$. The early attempts considered the ^{152}Gd nucleus as a spherical nucleus which follows the vibrational model [2] . Later, it has been proposed [8, 9] that these transitional nuclei should be regarded more in the framework of a rotational picture than a vibrational one. Other

Table 3. Results of ^{152}Gd gamma-gamma coincidence measurements (x means real coincidence, and N means unobserved coincidence in present study).

Gate	271.1	344.5	410.9	585.9	779.0
271.1		x			
314.0		x			
325.1		x			
344.5	x		x	x	x
352.0				x	
367.8		x	x		
410.0		x			
493.6	x	x			
503.2	x	x		x	
511.2					
519.6		x			x
533.9		N			
585.9		x			
678.4		x	x		
713.2	x	x	x	x	
764.8		x			
779.0		x			
795.0					
931.0					
974.5		x	x		
991.0	x	x			
1089.9		x			
1206.0		x			
1261.3		x			
1299.3		x			

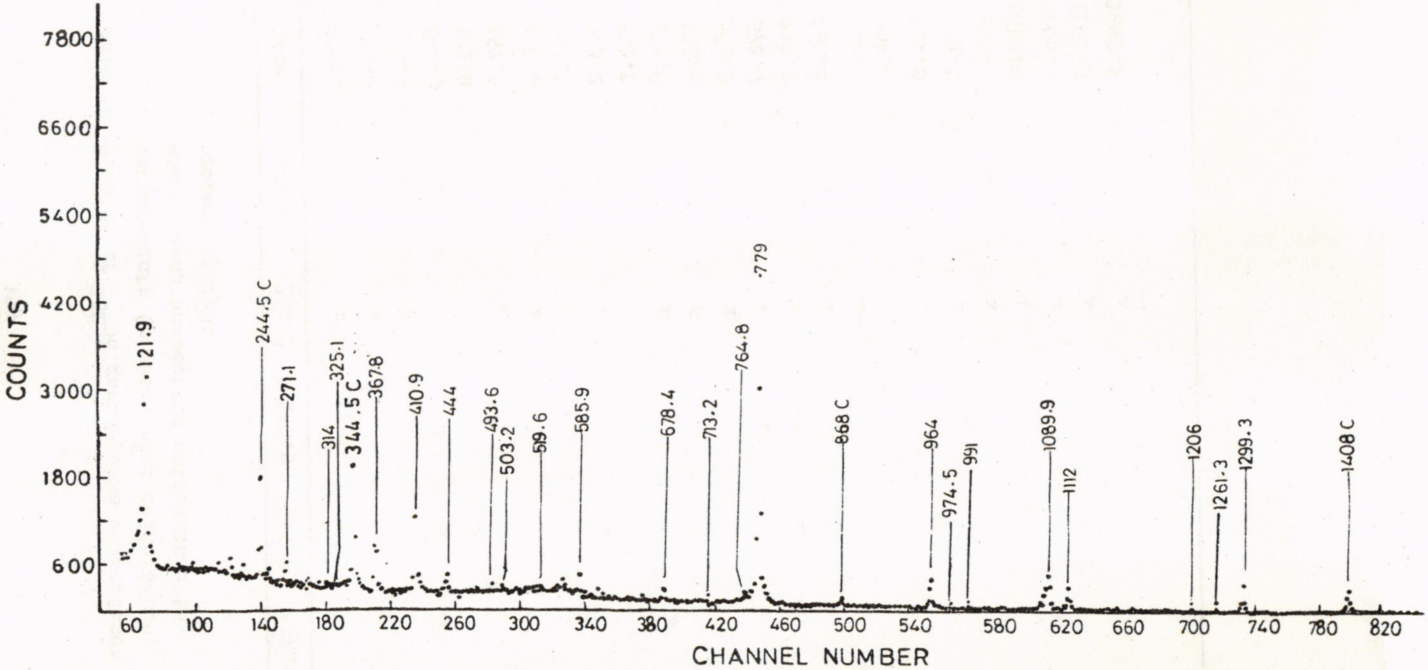

FIG.(1) GAMMA RAY SPECTRUM OF Eu^{152} IN COINCIDENCE WITH 344.5keV TRANSITION

ENERGIES SUFFIXED BY C ARISE FROM CHANCE COINCIDENCE

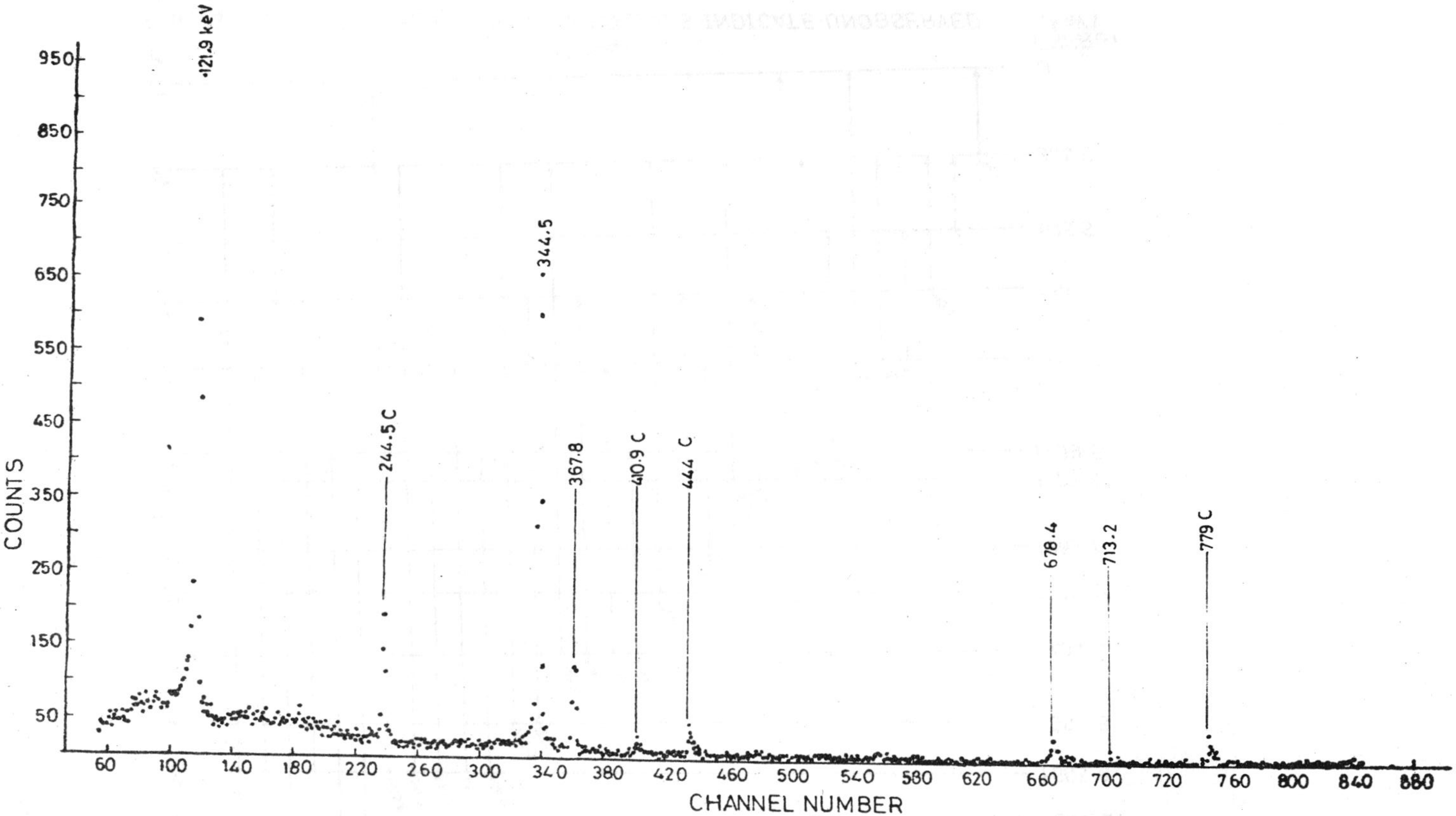

FIG.(.2.) GAMMARAY SPECTRUM OF Eu^{152} IN COINCIDENCE WITH 410.9 KeV TRANSITION
ENERGIES SUFFIXED BY C ARISE FROM CHANCE COINCIDENCE

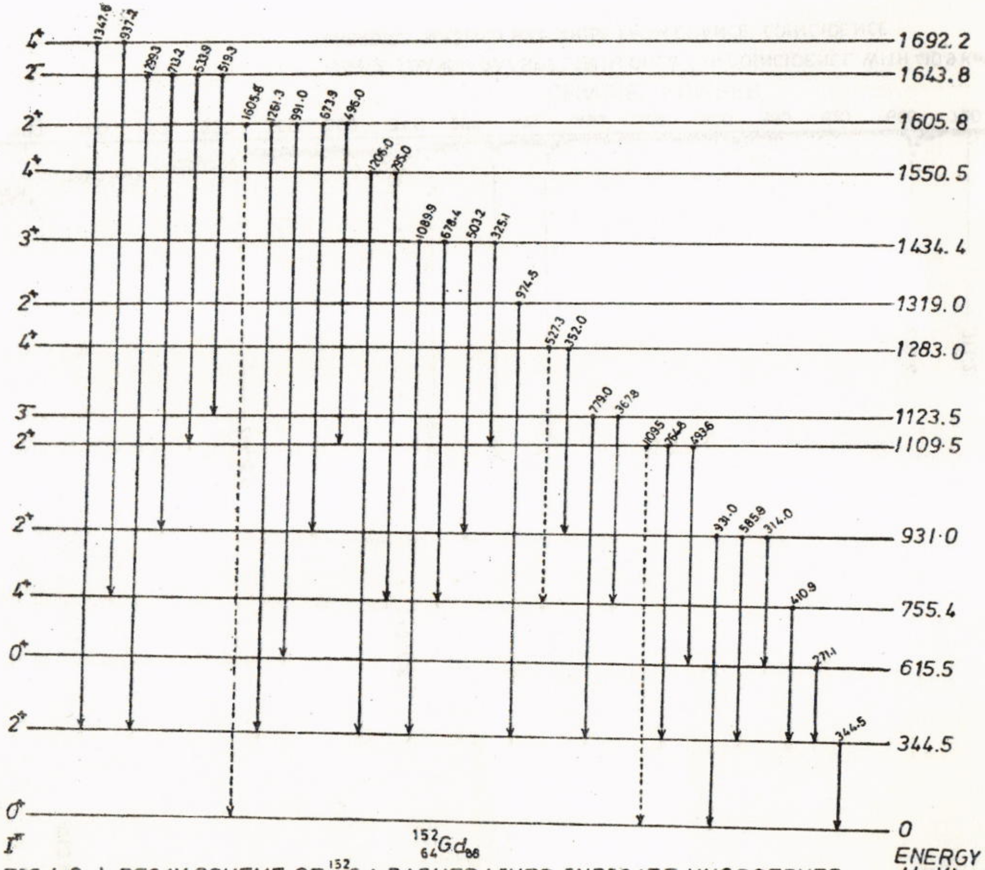

FIG.(3) DECAY SCHEME OF ^{152}Gd. DASHED LINES INDICATE UNOBSERVED TRANSITIONS nuclear reactions, like ^{150}Sm (α, 2n) ^{152}Gd and ^{153}Eu(p,2n) ^{152}Gd, support the presence of a g.s. rotational band up through spin of 10, with the 344.5 and 755.4 keV states as the first and second excited states of this band [15] . A comparison between the transitional ^{152}Gd states and the states of the deformed ^{152}Sm nucleus shows that both nuclei display a rotational nature (Fig. 4). As a result of these arguments, the rotational description for the states of ^{152}Gd nucleus is adopted in the discussion below. Figure 5 illustrates the main bands of ^{152}Gd which are described below.

A. Ground-State Rotational Band

The energy levels at 0, 344.5, and 755.4 keV have spins and parities 0^+ , 2^+ & 4^+ respectively, these are the members of the g.s. rotational band with $K^\pi = 0^+$. The VMI softness parameter [10] calculated from these levels is found to be equal to 2530 which indicates that ^{152}Gd is an extremely "soft" nucleus which has a very small moment of inertia due to its transitional nature.

B. Beta-Vibrational Band

The energy levels at 615.5, 931, and 1283 keV have the spins and parities 0^+ , 2^+ & 4^+ respectively. They belong to the beta-vibrational band with $K^\pi = 0^+$. These are rotational levels built on a beta vibrational energy with $\hbar w$ = 615.5 keV.

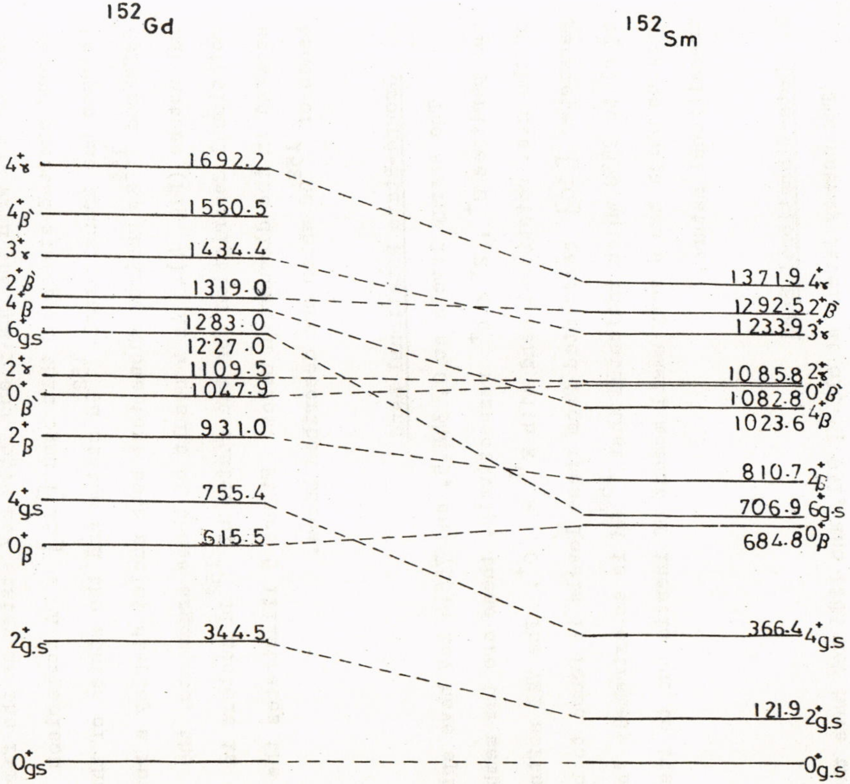

FIG.(4) COMPARISON OF THE LEVEL SCHEMES OF ^{152}Gd AND THOSE OF ^{152}Sm (ONLY POSITIVE PARITY LEVELS ARE CONSIDERED).

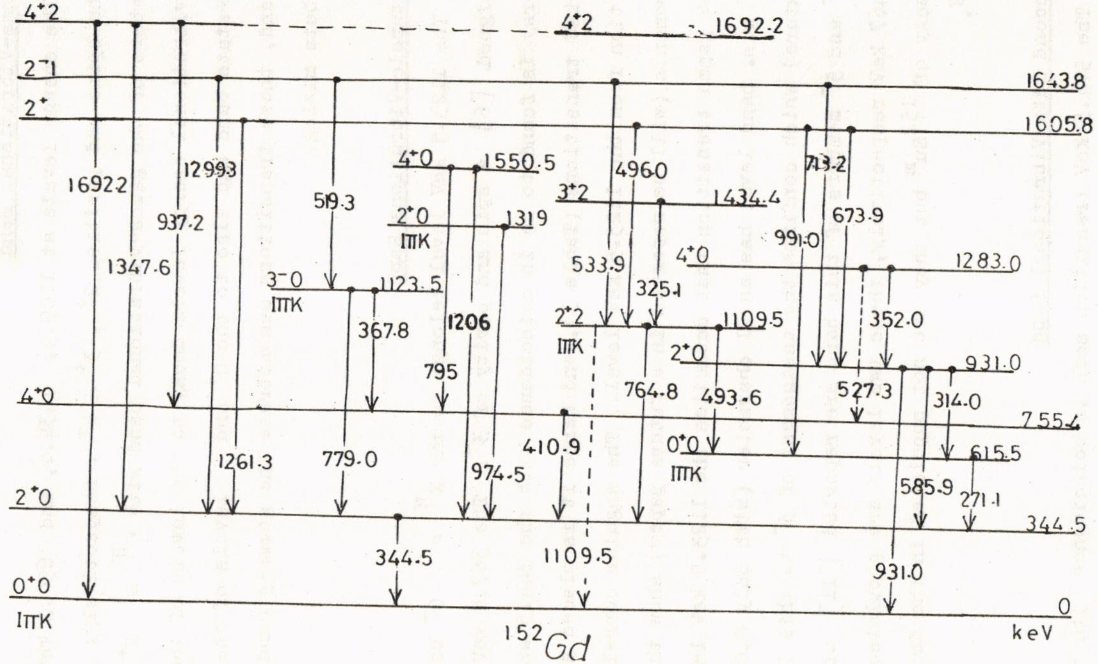

FIG. (5) BAND LEVEL SCHEME OF ^{152}Gd . DASHED LINES INDICATE UNOBSERVED TRANSITIONS.

C. Gamma-Vibrational Band

The energy levels at 1109.5, 1434.4, and 1692.2 keV have the spins and parities 2^+ , 3^+ & 4^+ , respectively; they are members of the gamma-vibrational band with $K^\pi = 2^+$. The gamma-vibrational energy levels decay to the levels of the ground-state band and also to the 0^+ and 2^+ levels of the beta band, these transitions demonstrate the gamma-ground and gamma-beta mixing.

D. Octupole-Vibrations Band

The 1123.5 keV level belongs to the $K^\pi = 0^-$ band, it is assigned [6] a spin and parity of 3^-. The 367.8 keV gamma-ray is found to be in coincidence with the 344.5 and 410.9 keV transitions (Table 3), and hence it is placed as a transition from the 1123.5 keV level. The angular correlation measurements (will be reported in a future paper) show that the 779 keV gamma transition that deexcites the 1123.5 keV level to the 2^+ g.s. band level has an E1 character (with only 0.09% of M2 mixture) which confirms the assignment of 3^- to this level. The 1^- and 5^- members of this band are reported [11] at 1314.6 and 1467 keV respectively, these two levels are populated in the decay of $^{152}Eu^m$ but they are not populated in the decay of $^{152}Eu^g$.

E. Second Beta-Vibrational Band

The 974.5 keV transition seen in coincidence with the 344.5 keV line (Table 3) confirms the 1319.0 keV level which was first reported [2] in the decay of ^{152}Tb. A weak 1206 keV line seen in coincidence with 344.5 keV establishes a level at 1550.5 keV, and it is also confirmed by the coincidence between the weak 795.0 keV line with the 410.9 keV gate (Table 3).

The two levels at 1319.0 and 1550.5 keV with the spins and parities 2^+ and 4^+ are considered as members of the second beta-vibrational band with $K^\pi = 0^+$. A third member of this band at 1047.9 keV and spin 0^+ is detected 11 in the decay of ^{152}Eu^m but it is not populated in the decay of ^{152}Eu^g.

F. Higher Energy States

(i) The 1643.8 keV level has been assigned spin and parity of 2^- on the basis of directional correlation [1, 12] and conversion coefficients measurements [13 , 14]. This state is believed to be a member of the $K^\pi = 1^-$ band.

(ii) The 2^+ level at 1605.8 keV is confirmed in the present investigation by the coincidence results (see Table 3), while it has been placed before [11] by energy fit alone. The nature of this level is not very clear, it might be a broken pair (quasi-particle) level.

CONCLUSIONS

The investigation of the decay of $^{152}Eu^{g}$ has confirmed the existence of 33 gamma transitions in the decay of ^{152}Gd, and the coincidence results have shown the presence of thirteen excited states in the decay scheme of ^{152}Gd. The energy levels at 1283.0, 1319.0 and 1692.2 keV are confirmed, in the present study, on the basis of coincidence results while they have been placed before by energy fit alone. The qualitative study of the characteristics of the structure of ^{152}Gd states seems to confirm that this nuclide has rotational characteristics more than vibrational nature as it has been suggested before. The comparison of the excited states in ^{152}Gd with those of the deformed ^{152}Sm nuclide confirms the rotational nature of ^{152}Gd. A second beta-vibrational band is found in ^{152}Gd at the energies 1319.0 and 1550.5 keV, with a missing 0^{+} member which has been detected in the decay of $^{152}Eu^{m}$. The nature of the higher energy levels are still not very clear and some of them might be quasi-particle levels.

REFERENCES

1. R. Bloch, B. Elbek and P.G. Tjom; Nucl. Phys. A 91, 576 (1967).
2. K. Gromov, Y.A. Kwznetzov, V.V. Kuznetsova, M.Y.A. Fenger, and M. Urbanes; Nucl. Phys. A 99, 588 (1967).
3. Nuclear Data Sheete (1964) 5-6-37, 1479.
4. L.L. Reidinger, N.R. Johnson and J.H. Hamilton; Phys. Rev. C 2, 2358 (1970).
5. L. Varnell, J.D. Bowman and J. Tresehuk; Nucl. Phys. A. 127, 270 (1969).
6. K.R. Baker, J.H. Hamilton and A.V. Ramyya; Z. Physik 256, 387 (1972).
7. B.A. Bishara, M.A. Al-Jeboori and K.F. Kaddoumi, Mustansiriyah J.Sc., 4 (1979).
8. M. Sakai; Nucl. Phys. A 104, 301 (1962).
9. R.K. Sheline; Phys. Rev. 150, 964 (1960).
10. M.A.J. Mariscotti, G. Scharff-Goldhaber and B. Buck; Phys. Rev. 178 No. 4, 1864 (1969).
11. J. Barrette, M. Barrette, A. Boutard, G. Lamoureux, S. Monaro, and Z. Markiza; Can. J. Phys. 49, 2462 (1971).
12. A.K. Grabowskiz; Ark. Fysik. 20, 177 (1961).
13. K.M. Bisgard, N.B. Nielsen and I. Soderman; Phys. Lett. 7, 57 (1963).
14. J.S. Larsen, O.Skilbreid and L. Visiren; Nucl. Phys. A100, 248 (1967).
15. Y. Gono, M. Ishihara and M. Sakai; Proc. Intr. Symp. Nucl. Struct. Contrib, Dubna (1964).

مجلة
علوم المستنصرية

كانون الأول ١٩٧٩

رقم الايداع في المكتبة الوطنية ببغداد ٢٧٢ لسنة ١٩٧٩

مجلة علوم المستنصرية

المجلد ٤ ، العدد ٢ ، كانون الاول ١٩٧٩

كلية العلوم — الجامعة المستنصرية — بغداد — العراق —

تعليمات للمؤلفين

١. تقدم ثلاث نسخ من البحث مطبوعة على الآلة الكاتبة وعلى ورق ابيض صقيل وتترك مسافة ٢,٥ سم على يسار كل صفحة .

٢. تقدم خلاصة باللغة العربية وأخرى باللغة الانكليزية وتطبع كل منهما على ورقة منفصلة .

٣. يطبع عنوان البحث وكذلك اسم المؤلف (او المؤلفين) وعنوانه على ورقة منفصلة ويكتب اسم المؤلف كاملا كان يكتب (احمد م. علي) .

٤. تقدم الرسوم التوضيحية منفصلة عن مسودة البحث وترسم بالحبر الصيني الاسود على ورق شفاف وترفق ثلاث صور لكل رسم وتكتب عناوين الرسوم على نفس الورقة .

٥. تنظم الجداول باسلوب تجعلها مفهومة دون اللجوء الى النص وذلك باعطاء كل جدول وكل عمود وصفا واضحا .

٦. لايجوز اعطاء المعلومات ذاتها بالرسم وبالجدول في وقت واحد الا اذا اقتضت ضرورة النقاش ذلك .

٧. يشار الى المصدر برقم ضمن قوسين [بعد الجملة مباشرة وتطبع كافة المصادر على ورقة منفصلة ويتوجب عند ذكر مختصرات اسماء المجلات اتباع اسلوب

٨. من المحبذ حيثما كان ممكنا ان يتسلسل البحث ليتضمن المقدمة ، طرق التجربة ، النتائج ، المناقشة.

مجلة

علوم المستنصرية

طالب

المجلد ٤ العدد ٢ كانون الاول ١٩٧٩

مطبعة كلية العلوم - جامعة بغداد