

excited state of a molecule is lowered to a greater extent as compared to the ground state in such solvents, the red shift is understandable. In α -hydroxyketones this kind of red shift has been observed¹⁵. The spectra in Fig. 1 show that the effect due to stability of polar states dominates in the present system and the red shift increases with the dielectric constant of the medium. A detailed analysis is, however, not possible, since the charge distribution is expected to be affected by even hydrogen bonding and if it leads to increased dipole moment, the expected blue shift due to hydrogen bonding may get cancelled¹⁶. The contribution of the polar structure is further apparent from the results presented in Table 1. The oscillator strength (f) continuously increases with the dielectric. A linear relationship is observed between the transition energies and the dielectric constant of the medium. With increase in polarity, the separation between the two concerned electronic states decreases. In terms of Franck-Condon principle excitation from a solvated ground state leads not to the energetically most stable solvated conformation of the excited state, but to a conformation geometrically identical to the solvated ground state¹⁷. Thus in the transition a change in the solvation energy can result leading to decreased separation between the ground and the excited state as observed.

Now band-II can be assigned to $\pi^* \leftarrow \pi$ transition. It undergoes a red shift with the increase in polarity of the medium; it is of higher energy than $\pi^* \leftarrow n$ transition and it is of higher intensity than band-I (as expected¹⁸) when solute-solvent interactions are minimum.

Another interesting feature is that the (f) value for $\pi^* \leftarrow n$ transition is of the order of 10^{-2} , while in normal cases it is of the order of 10^{-3} to 10^{-4} . This could be due to the symmetry of various states being modified by vibrational interactions particularly because of the allowed and forbidden excited states

being close¹⁹. The $\pi^* \leftarrow n$ transition in the present case is only ~ 15 kcal below $\pi^* \leftarrow \pi$ transition and the (f) value for band-II is lower than that for band-I in methylcyanide (Table 1). Furthermore, the bands are closer in this solvent which demonstrates the possible contribution of polar states and mixing of states.

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TABLE 1 — ENERGIES AND OSCILLATOR STRENGTH (f) OF ABSORPTION BANDS(a)

Dielectric constant(b)	Band-I		Band-II	
	Energy kcal mole ⁻¹	(f)(c) $\times 10^2$	Energy kcal mole ⁻¹	(f) $\times 10^2$
	CYCLOHEXANE			
2.02	116.7	2.975	132.9	4.537
	METHANOL			
32.63	114.6	4.062	132.6	(d)
	METHYL CYANIDE			
36.70	114.0	4.441	125.9	2.511
	WATER			
80.00	112.1	6.479	127.6	7.929

(a) Spectra were recorded at $25^\circ \pm 2^\circ$. (b) Values of the dielectric constants were taken from *Handbook of chemistry* (Longmans, New York), 1957. (c) Oscillator strengths are calculated from the absorption bands and their widths at half height. (d) Diffused band.

High Temperature Thermal Expansion Studies of Pure UO_2 , Gd_2O_3 & of UO_2 -1.5 w/o Gd_2O_3 Solid Solution

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Thermal expansions of pure UO_2 , Gd_2O_3 (C-type) and UO_2 -1.5 w/o Gd_2O_3 solid solution have been measured employing high temperature X-ray diffractometry in the range 298-1700 K in pure helium atmosphere. The results show that the coefficient of linear thermal expansion of pure UO_2 is higher than that of Gd_2O_3 (C-type) or urania-gadolinia solid solution.

URANIUM dioxide (UO_2) has a face-centred cubic structure and is known¹ to form a single phase cubic fluorite type solid solution with Gd_2O_3 up to

a composition of about 40 m/o Gd_2O_3 . The cell parameters of UO_2 - Gd_2O_3 fluorite type cubic solid solutions vary linearly with composition. Gd_2O_3 is known to exist in two forms¹⁻³.

Many investigators⁴ have studied the high temperature physical properties of UO_2 . The high temperature thermal expansion properties of pure UO_2 are also well known^{5,6}. However, limited data^{2,7} exist in the literature on the thermal expansion properties of pure Gd_2O_3 and UO_2 - Gd_2O_3 solid solutions.

The present investigation deals with the thermal expansion measurements of pure UO_2 , Gd_2O_3 (C-type) and UO_2 -1.5 w/o Gd_2O_3 solid solution, employing high temperature X-ray diffractometry in the range 298-1700K in pure helium atmosphere, and reports the cell parameters in the range up to 1700K in the case of UO_2 and UO_2 -1.5 w/o Gd_2O_3 solid solution and 1575K in case of pure Gd_2O_3 (C-type).

Natural UO_2 and natural UO_2 -1.5 w/o Gd_2O_3 of nuclear purity were obtained from the Atomic Fuels Division (BARC). Pure Gd_2O_3 (C-type) was obtained from the Pure Materials Section of this Division.

MRC model X-86-N3 high temperature X-ray diffractometer attachment mounted on a Philips wide angle goniometer was used. The details of this have been described elsewhere⁸.

The cell parameters of all the three substances under study vary linearly with temperature (Fig. 1).

The per cent linear thermal expansion was evaluated from cell parameter measurements. The linear variation of cell parameters and of per cent linear thermal expansion could be expressed by the following least square fitted equations.

UO_2 (temperature range 298-1700K):

$$a_T = 0.5452 \pm 0.00015 + 5.5402 \times 10^{-6}T \quad \dots(1)$$

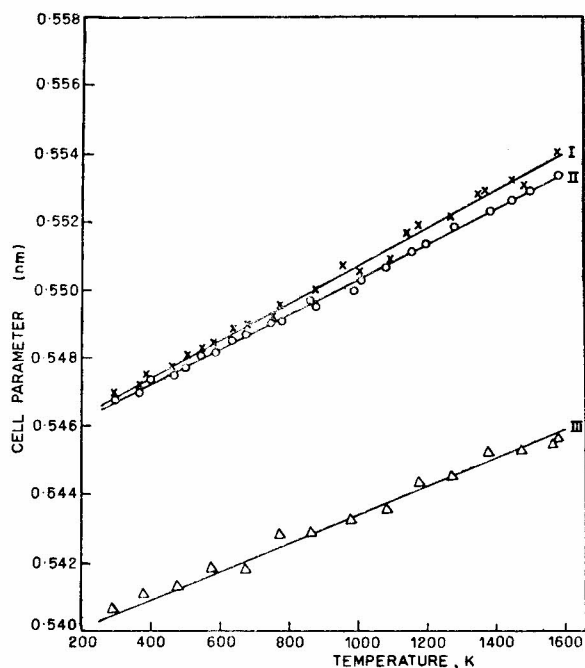


Fig. 1 — Variation of cell parameters with temperature for (I) UO_2 , (II) UO_2 -1.5 w/o Gd_2O_3 and (III) Gd_2O_3 (C-type) in pure helium atmosphere

$$\% \text{ exp} = -0.310 \pm 0.028 + 10.128 \times 10^{-4}T \quad \dots(2)$$

Gd_2O_3 (C-type) (temperature range 298-1575K):

$$a_T = 0.5393 \pm 0.00028 + 4.1570 \times 10^{-6}T \quad \dots(3)$$

$$\% \text{ exp} = -0.218 \pm 0.027 + 7.433 \times 10^{-4}T \quad \dots(4)$$

UO_2 -1.5 w/o Gd_2O_3 solid solution (temperature range 298-1700K):

$$a_T = 0.5452 \pm 0.00009 + 5.1849 \times 10^{-6}T \quad \dots(5)$$

$$\% \text{ exp} = -0.296 \pm 0.016 + 9.476 \times 10^{-4}T \quad \dots(6)$$

where a_T is the cell parameter in (nm) at T K.

The values of the coefficients of average linear thermal expansion ($\alpha_1 \times 10^6 K^{-1}$), of UO_2 , Gd_2O_3 and UO_2 -1.5 w/o Gd_2O_3 in the temperature range described above are 10.07, 7.43 and 9.38.

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Viscosity Behaviour of Aqueous Solutions of Sodium Chloroacetate & α -Chloropropionate

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Viscosities of aqueous solutions of sodium chloroacetate and sodium α -chloropropionate have been measured at 25° in the concentration range 0.02-0.4 mol dm^{-3} . Using Jones-Dole equation, A and B coefficients have been determined. The results are discussed in terms of ion-solvent interactions.

STUDIES on concentration and temperature dependence of viscosity of aqueous electrolyte solutions¹ have provided many useful insights into the extent of ionic hydration^{2,3} and into structural interactions^{1,4} within the ionic hydration cospheres^{5,6}. The viscosity B coefficient of the Jones-Dole⁷ equation and its variation with temperature has also provided information on the structure-making or structure-breaking property of an ion in solution. However, similar studies on large sized anions are lacking. This prompted us to study the anion-water interaction by carrying out viscosity measurements