

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):

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

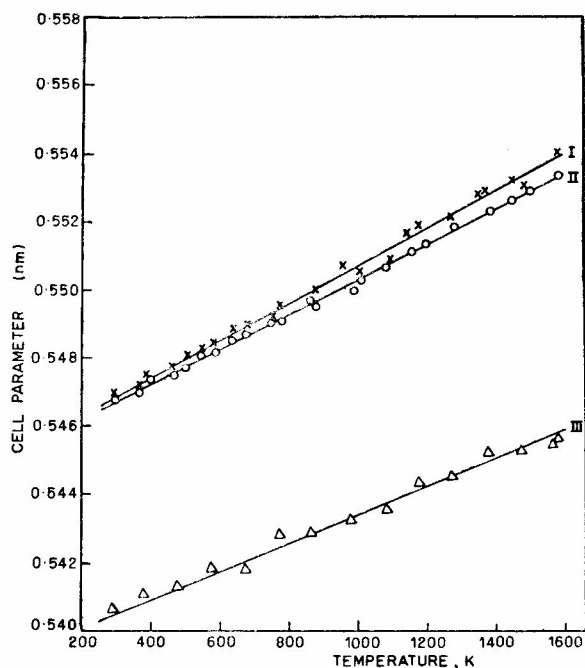


Fig. 1 — Variation of cell parameters with temperature for (I) UO_2 , (II) UO_2 -1.5 w/o Gd_2O_3 and (III) Gd_2O_3 (C-type) in pure helium atmosphere

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

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.

References

- BEALS, R. J., HANDWERK, J. H. & WORNA, B. J., *J. Am. ceram. Soc.*, **52** (1969), 578.
- SAWBRIDGE, P. T. & WATERMAN, N. A., *J. material Sci.*, **3** (1968), 15.
- ROTH, R. S. & SCHNEIDER, S. J., *J. res. NBS*, **64A** (1960), 309.
- BELLE, J., *Uranium dioxide, properties and nuclear applications* (Naval Reactors, Division of Reactor Development, United States Atomic Energy Commission), 1961.
- HOCH, M. & MOMIN, A. C., *High Temperatures-High Pressures*, **1** (1969), 401.
- BALDOCK, P. J., SPINDLER, W. E. & BAKER, T. W., *J. nucl. Material*, **18** (1966), 305.
- WADA, T., NORO, K. & TSUKUI, K., paper No. 63 in the Proceedings of the International Conference, London organized by the British Nuclear Energy Society, 15-19 October 1973.
- MOMIN, A. C., MATHEWS, M. D. & KARKHANAVALA, M. D., *Indian J. Chem.*, **9** (1971), 582.

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

of sodium chloroacetate⁸ and sodium α -chloropropionate⁸ in water at 25°.

All solutions were prepared on molar basis in doubly distilled water and were deaerated. The time of flow measurements on solutions were made using Tuan and Fuoss⁹ type viscometer having a flow time of 717.6 sec for water at 25° in a thermostat with temperature fluctuations less than $\pm 0.005^\circ$. Prior to the measurements, the viscometer was calibrated using 20% sucrose solution at 25°. The density measurements were carried out using 25 ml calibrated pycnometer. The accuracy in density measurement was of the order of 5×10^{-5} g/cc.

The data were analysed in terms of Jones-Dole equation⁷. The values of A and B coefficients were 0.004 and 0.208 dm³ mol⁻¹ for sodium chloroacetate and 0.004 and 0.508 dm³ mol⁻¹ for sodium α -chloroacetate respectively at 25°. It is observed that values of A -coefficient in the present case are positive and equal which is in accordance with the behaviour of 1:1 electrolytes and in confirmation with the Debye-Hückel theory. The B -coefficients are found to be positive for both the salts and it is larger for sodium α -chloropropionate as compared to sodium chloroacetate. Since B -coefficient is an additive property, one can calculate the ionic B -coefficient. Subtracting the value for sodium ion as (0.086 dm³ mol⁻¹)¹⁰, the individual ionic B -coefficient for chloroacetate (CH₂ClCOO⁻) and the α -chloropropionate (CH₃CHClCOO⁻) obtained are 0.1220 and 0.4220 dm³ mol⁻¹ respectively.

The value of B -coefficient for acetate ion (0.25) reported by Laurence and Wolfenden¹¹ has been interpreted by Gurney⁵ as not due to partial localization of negative charge over the entire acetate ion, thereby rendering it a structure-forming ion. In the presently studied chloroacetate ion, the heavy and large size of chlorine atom makes the ion more polarizable as also the negative charge may spread all over the ion. Hence one expects a smaller B -coefficient value for the chloroacetate ion and it is indeed the case. Further, it has been established that introduction of an hydrophobic group (-CH₂-) in an ion¹² or in a molecule¹³ results in a more positive B -coefficient. This fact corroborates with the large B -coefficient (0.42) obtained for α -chloropropionate ion. It appears that a large increase in hydrophobic surface of the ion results in a feeble ionic charge and enforcement of water structure around the large size anions.

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References

1. STOKES, R. H. & MILLS, R., *Viscosity of electrolytes and related properties* (Pergamon Press, Oxford), 1965.
2. NIGHTINGALE, E. R., cited in *Chemical physics of ionic solutions*, edited by B. E. Conway & R. G. Barradas (John Wiley, New York), 1966.
3. KAMINSKY, M., *Discuss Faraday Soc.*, **24** (1957), 133.
4. DESNOYERS, J. & PERRON, G., *J. soln Chem.*, **1** (1972), 199.
5. GURNEY, R. W., *Ionic processes in solutions* (McGraw-Hill, New York), 1953.
6. DESNOYERS, J., AREL, M., PERRON, G. & JOLICOUR, C., *J. phys. Chem.*, **73** (1969), 3346.
7. JONES, G. & DOLE, M., *J. Am. chem. Soc.*, **51** (1929), 2950.

8. BANERJEE, K., *Viscosity and volumetric behaviour of aqueous solutions of sodium salts of chlorosubstituted fatty acids*, Dissertation, Nagpur University, Nagpur, 1975.
9. TUAN, D. F. T. & FUOSS, R. M., *J. phys. Chem.*, **67** (1963), 1343.
10. COX, W. M. & WOLFENDEN, J. M., *Proc. roy. Soc.*, **A145** (1934), 475.
11. LAURENCE, V. D. & WOLFENDEN, J. M., *J. chem. Soc.*, (1934), 1114.
12. KAY, R. L., VITUCCIO, T., ZAWOYSKI, C. & EVANS, D. F., *J. phys. Chem.*, **70** (1966), 2336.
13. HERSKOVITZ, T. T. & KELLY, T. M., *J. phys. Chem.*, **77** (1973), 381.

Viscosity of Ternary Electrolytes in Dioxane-Water Mixtures

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The viscosity and density data of seventeen electrolytes in 10, 20 and 30% (by wt) in dioxane-water mixtures have been analysed. The values of the B coefficient and V_e , the effective rigid molar volume have been found to increase with the increase in dioxane content in the medium. This increase occurs due to the formation of more and more hydrogen bonded dioxane-water molecules, with the increase in dioxane content.

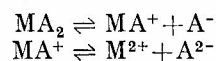
THE viscosity data of electrolyte solution in aqueous and non-aqueous media can be analysed in terms of modified Jones-Dole equation¹,

$$\eta_r = 1 + AC^{1/2} + BC^x \quad \dots(1)$$

where x is an empirical constant and is near about unity, and by Eq. (2) proposed by Das²,

$$\eta_r = 1 + A(\alpha C)^{1/2} + B_i \alpha C + B_{ip}(1 - \alpha C) \quad \dots(2)$$

For an electrolyte,



If α is the degree of dissociation of MA⁺, then, Eq. (2) can be written as

$$\eta_r = 1 + A(\alpha C)^{1/2} + B_{A^-}(1 + \alpha C) + B_{M^{2+}}\alpha C + B_{MA^+}(1 - \alpha C) \quad \dots(3)$$

$$\text{or } \eta_r - 1 - A(\alpha C)^{1/2} = (B_{MA^+} + B_{A^-}) + \alpha(B_{M^{2+}} + B_{A^-} - B_{MA^+}) \quad \dots(4)$$

The plot of LHS vs α should have a slope of $(B_{M^{2+}} + B_{A^-} - B_{MA^+})$ and an intercept at $\alpha = 0$, of $(B_{MA^+} + B_{A^-})$ and at $\alpha = 1$, the intercept is $(B_{M^{2+}} + 2B_{A^-})$, since there is 1:0 ion pair formation. Hence B could be computed at $\alpha = 1$.

Fuoss and coworkers^{3,4} have confirmed Einstein's equation⁵:

$$B = 2.5V \quad \dots(5)$$

where V is the molal volume of the solute particles. Kurusev *et al.*⁶ reported that Eq. (5) is valid for ions of radii $> 5 \text{ \AA}$. Breslau and Miller⁷ designate V as the effective rigid molar volume, V_e and