Heats of Solution of Uranyl Nitrate Dihydrate in Methanol & Ethanol

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The heats of solution of $UO_2(NO_3)_2.2H_2O(c)$ in methanol and ethanol are −34·3 and −19.3 KJ mol^{-1}, restively at 303°K. The heats of solution of $UO_2(NO_3)_2.2CH_3OH(c)$ in methanol and $UO_2(NO_3).2C_2H_5OH(c)$ in ethanol are −11·7 and −15·8 KJ mol^{-1}, respectively. The standard heats of formation of $UO_2(NO_3)_2.2CH_3OH(c)$ and $UO_2(NO_3)_2.2C_2H_5OH(c)$ are −1935·4 and −1993·2 KJ mol^{-1}, respectively. The mean bond dissociation energies between uranium and oxygen (alcohol) bonds are 77·8 and 72·9 KJ mol^{-1}, respectively.

THE two water molecules in uranyl nitrate dihydrate $UO_2(NO_3)_2.2H_2O$ are coordinated to uranium forming uranium-oxygen bonds in the *trans*-position to the two bidentate nitrate groups[1]. $UO_2(NO_3)_2.2H_2O(c)$ dissolves completely in methanol and ethanol and the solution on evaporation yields crystalline uranyl nitrate *bis*-alcohol, $UO_2(NO_3)_2.2ROH(c)$, where R is the alkyl radical[2]. In the present study we report values for the heats of solution of $UO_2(NO_3)_2.2H_2O(c)$ in methanol and ethanol, of $UO_2(NO_3)_2.2CH_3OH(c)$ in methanol and of $UO_2(NO_3)_2.2C_2H_5OH(c)$ in ethanol. The standard heats of formation of $UO_2(NO_3)_2.2CH_3OH(c)$ and $UO_2(NO_3)_2.2C_2H_5OH(c)$ have been calculated and uranium-oxygen (alcohol) bond strength estimated.

Uranyl nitrate hexahydrate (BDH, AR) was desiccated over 70% H_2SO_4 for 3 days to form uranyl nitrate trihydrate which on further dehydration over conc. H_2SO_4 at room temperature in a vacuum desiccator for 7 days[3,4] yielded uranyl nitrate dihydrate [Found: U, 55·1; N, 6·4. Calc. for $UO_2(NO_3)_2.2H_2O$: U, 55·3; N, 6·5%). The crystalline dihydrate when dissolved in pure and dry methanol or ethanol, prepared fresh gave a clear greenish-yellow solution which on evaporation under reduced pressure and at ice-temperature yielded crystalline uranyl nitrate *bis*-methanol-ethanol, $UO_2(NO_3)_2.2ROH$ [Found: U, 49·3; N, 6·01. Calc. for $UO_2(NO_3)_2.2CH_3OH$: U, 51·9; N, 6·11%. Found: U, 50·4, N, 5·68. Calc. for $UO_2(NO_3)_2.2C_2H_5OH$: U, 48·9, N, 5·8%].

Uranium was analysed by the oxinate method and nitrogen by the Duma's method. Attempts to prepare similar adducts with isopropanol failed as the dihydrate is spraingly soluble in this solvent.

The heats of solution were measured in a closed-system calorimeter[5,6]. The temperature sensing element was a 10 kilo-ohm thermistor and a manganin heater was used for electrical calibration. The samples were sealed in fragile bulbs which on rupturing mixed rapidly with the calorimeter liquid.

TABLE 1 — HEATS OF SOLUTION OF URANYL NITRATE DIHYDRATE AND URANYL NITRATE *bis*-ALCOHOL IN METHANOL AND ETHANOL AT 303°K

(Values in KJ mol^{-1})

Compound	Weight (g)	Conc. *M*	ΔH_3	ΔH_5
	SOLVENT: MeOH(l) (125 ml)			
$UO_2(NO_3)_2.2H_2O(c)$	0·94560 1·26285 1·27620	0·017592 0·023490 0·023740	−34·3 −34·3 −33·7	
		Av =	−34·4 ±0·2	
		2H O(c)		
	EtOH (125 ml)			
$UO_2(NO_3)_2.2H_2O(c)$	0·48640 1·13830 1·59688	0·009048 0·021177 0·029708	−19.4 −19·4 −19·3	
		Av =	−19·4 ±0·1	
	MeOH (125 ml)			
$UO_2(NO_3)_2.2CH_3OH(c)$	0·54370 0·78230 0·86005	0·009496 0·013664 0·015022		−12·9 −11·4 −10·9
			Av =	−11·7 ±0·3
	EtOH (125 ml)			
$UO_2(NO_3)_2.2C_2H_5OH(c)$	0·2725 0·6838 1·0589	0·004484 0·011255 0·018496		−16·4 −15·2 −15·8
			Av =	−15·8 ±0·5

Anhydrous uranyl nitrate is difficult to prepare. An indirect method[7] employing the following thermodynamic cycle has been used for the calculation of heats of reaction of $UO_2(NO_3)_2(c)$ with alcohol, $ROH(l)$, to form $UO_2(NO_3)_2.2ROH(c)$.

In the above reactions, ΔH_3 and ΔH_5 have been determined experimentally and the values are listed in Table 1. For the heat of reaction of $UO_2(NO_3)_2(c)$ with $2H_2O(l)$ (Eq. 2), we have used the value[8] −58·6 KJ mol^{-1}. The dilution of a large volume of alcohol containing a small amount of dissolved uranyl nitrate complex with a small amount of alcohol would have no thermal influence upon ΔH_4 and has, therefore, been neglected. The heat of solution of water in excess of alcohol has

$$UO_2(NO_3)_2(c)+2ROH(l) = UO_2(NO_3)_2.2ROH(c);\ \Delta H_1 \quad \ldots(1)$$

$$UO_2(NO_3)_2(c)+2H_2O(l) = UO_2(NO_2)_2.2H_2O(c);\ \Delta H_2 \quad \ldots(2)$$

$$UO_2(NO_3)_2.2H_2O(c)+mROH(l) = UO_2(NO_3)_2.2ROH\ [\text{in } (m-2)ROH,H_2O \text{ soln}];\ \Delta H_3 \quad \ldots(3)$$

$$UO_2(NO_3)_2.2ROH\ [\text{in } (m-2)ROH,\ 2H_2O \text{ soln}]+2ROH(l) = UO_2(NO_3)_2 2ROH\ [\text{in } mMROH,\ 2H_2O \text{ soln}];\ \Delta H_4 \quad \ldots(4)$$

$$UO_2(NO_3)_2.2ROH(c)+mROH(l) = UO_2(NO_3)_2.2ROH\ [\text{in } mROH \text{ soln}];\ \Delta H_5 \quad \ldots(5)$$

$$UO_2(NO_3)_2.2ROH\ [\text{in } mROH \text{ soln}]+2H_2O(l) = UO_2(NO_3)_2.2ROH\ [\text{in } mROH,\ 2H_2O \text{ soln}];\ \Delta H_6 \quad \ldots(6)$$

$$\text{Hence, } \Delta H_1=\Delta H_2+\Delta H_3+\Delta H_4-\Delta H_5-\Delta H_6 \quad \ldots(7)$$

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been interpolated from the data[8,9] reported in the literature assuming that the presence of uranyl nitrate *bis*-alcohol will have no effect on the heat of solution. ΔH_6 thus estimated for methanol and ethanol complexes, respectively, are 0·42 and 1·5 KJ mol^{-1}. Hence ΔH_1 for $UO_2(NO_3)_2.2CH_3OH(c)$ and $UO_2(NO_3)_2.2C_2H_5OH(c)$ are $-80{\cdot}8$ and $-60{\cdot}6$ KJ mol^{-1}, respectively.

Standard heats of formation of uranyl nitrate bis-alcohols — The heats of formation of the *bis*-alcohol compounds have been calculated from the relation (8).

$$\Delta H_1 = \Sigma\Delta H_f^\circ \text{ (products)} - \Sigma\Delta H_f^\circ \text{ (reactants)} \quad \ldots(8)$$

Therefore

$$\Delta H_f^\circ UO_2(NO_3)_2.2ROH(c) = \Delta H_f^\circ UO_2(NO_3)_2(c) + 2\Delta H_f^\circ \, ROH(l) + \Delta H \quad \ldots(9)$$

By computing ΔH_f° $UO_2(NO_3)_2(c)$ from Lange[8] and ΔH_f° $ROH(l)$ from Cox and Pilcher[10], ΔH_f° $UO_2(NO_3)_2.2CH_3OH(c)$ and ΔH_f° $UO_2(NO_3)_2.2C_2H_5OH(c)$ come out to be $-1935{\cdot}4$ and $-1993{\cdot}2$ KJ mol^{-1}, respectively.

The mean bond dissociation energy of uranium-oxygen (alcohol) bond has been calculated from the following well-known[11] steps (10-14):

$$UO_2(NO_3)_2(c) + 2ROH(l) = UO_2(NO_3)_2.2ROH(c); \; \Delta H_1 \quad \ldots(10)$$

$$UO_2(NO_3)_2.2ROH(c) = UO_2(NO_3)_2.2ROH(g); \; \Delta H_s' \quad \ldots(11)$$

$$UO_2(NO_3)_2(c) = UO_2(NO_3)_2(g); \; \Delta H_s'' \quad \ldots(12)$$

$$2ROH(l) = 2ROH(g); \; 2\Delta H_v \quad \ldots(13)$$

$$UO_2(NO_3)_2(g) + 2ROH(g) = UO_2(NO_3)_2.2ROH(g); \; \Delta H_g \quad \ldots(14)$$

where $\Delta H_s'$ and $\Delta H_s''$ are the heats of sublimation of uranyl nitrate *bis*-alcohol and uranyl nitrate, respectively; ΔH_v, the heat of vaporization of the alcohol; and ΔH_g, is the gas-phase molecular dissociation energy. Whence, $\Delta H_g = \Delta H_1 + \Delta H_s' - \Delta H_s'' - 2\Delta H_v$.

As pointed out earlier[6] the heats of sublimation data are assumed to be the same for uranyl nitrate and the *bis*-complexes. Hence ΔH_g, for the *bis*-methanol and *bis*-ethanol are $-155{\cdot}6$ and $-145{\cdot}8$ KJ mol^{-1}; and the uranium-oxygen (alcohol) bond-strength, $E(O-U) = -\Delta H_g/2 = 77{\cdot}8$ and $72{\cdot}9$ KJ mol^{-1}, respectively for methanol and ethanol adducts. The values compare well with the alcohol and UCl_4 bond strength[11] in $UCl_4.4ROH$ and with the uranium-oxygen (water) bond strength reported earlier[12,13]. The bond strengths in *bis*-alcohol are stronger than the uranium-water bond strengths on account of the electron donating effect of the alkyl groups. It can be seen that the steric effect due to long-chain ethyl group slightly opposes the positive inductive effect of the ethyl group producing a lower bond strength in *bis*-ethanol.

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Viscosity & Apparent Molal Volume of Potassium Chloride in Acetone-, Dioxane- & Methyl Alcohol-Water Mixtures

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The viscosity and apparent molal volume of potassium chloride in acetone-, dioxane- and methyl alcohol-water mixtures containing 10, 20, 30, 40 and 50% (w/w) of the organic components have been measured at 35° and the data analysed in terms of Jones-Dole epuation. The values of the constants *A* and *B* of Jones-Dole equation and the apparent molal volume have been explained in terms of ion-ion and ion-solvent interactions.

Viscosity and apparent molal volume (ϕ) of electrolyte solutions in aquo-organic solvents have been studied with a view to understanding the nature of ion-ion and ion-solvent interaction respectively[1-11]. The viscosity and apparent molal volume of KCl in acetone-, dioxane- and methyl alcohol-water mixtures containing 10, 20, 30, 40 and 50% of the organic solvent have now been, measured at concentrations $<0{\cdot}1M$ at $35° \pm 0{\cdot}001°$.

KCl, acetone, dioxane and methyl alcohol used were of E. Merck (extra pure) qualities. Purification of the solvents and preparation of mixed solvents and solutions were carried out as reported earlier[12]. The procedures for viscosity measurement were the same as described by Prasad *et al.*[13]. The density measurements were made by pyknometer (50 ml) with buoyancy correction and the values are accurate up to 4 in 10^6. The concentration range was from 0·1 to $0{\cdot}001M$.

The applicability of the Jones-Dole equation[2] is shown by the linear plot of $\eta_r - 1/C^{\frac{1}{2}}$ versus $C^{\frac{1}{2}}$. The values of the constants A and B, given by the intercept and slope of the plots respectively are given in Table 1. The calculated B values are in acceptable agreement with those obtained from these plots.