

## Heats of Solution of Uranyl Nitrate Dihydrate in Methanol & Ethanol

LAMBODAR THAKUR\* &amp; MD FAIZ AHMAD

Department of Chemistry, Bhagalpur University  
Bhagalpur 812007

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The heats of solution of  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}(c)$  in methanol and ethanol are  $-34.3$  and  $-19.3$  KJ mol $^{-1}$ , respectively at 303°K. The heats of solution of  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{CH}_3\text{OH}(c)$  in methanol and  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{C}_2\text{H}_5\text{OH}(c)$  in ethanol are  $-11.7$  and  $-15.8$  KJ mol $^{-1}$ , respectively. The standard heats of formation of  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{CH}_3\text{OH}(c)$  and  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{C}_2\text{H}_5\text{OH}(c)$  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  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  are coordinated to uranium forming uranium-oxygen bonds in the *trans*-position to the two bidentate nitrate groups<sup>1</sup>.  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}(c)$  dissolves completely in methanol and ethanol and the solution on evaporation yields crystalline uranyl nitrate *bis*-alcohol,  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{ROH}(c)$ , where R is the alkyl radical<sup>2</sup>. In the present study we report values for the heats of solution of  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}(c)$  in methanol and ethanol, of  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{CH}_3\text{OH}(c)$  in methanol and of  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{C}_2\text{H}_5\text{OH}(c)$  in ethanol. The standard heats of formation of  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{CH}_3\text{OH}(c)$  and  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{C}_2\text{H}_5\text{OH}(c)$  have been calculated and uranium-oxygen (alcohol) bond strength estimated.

Uranyl nitrate hexahydrate (BDH, AR) was desiccated over 70%  $\text{H}_2\text{SO}_4$  for 3 days to form uranyl nitrate trihydrate which on further dehydration over conc.  $\text{H}_2\text{SO}_4$  at room temperature in a vacuum desiccator for 7 days<sup>3,4</sup> yielded uranyl nitrate dihydrate [Found: U, 55.1; N, 6.4. Calc. for  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ : 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,  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{ROH}$  [Found: U, 49.3; N, 6.01. Calc. for  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{CH}_3\text{OH}$ : U, 51.9; N, 6.11%. Found: U, 50.4, N, 5.68. Calc. for  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$ : 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 sparingly soluble in this solvent.

The heats of solution were measured in a closed-system calorimeter<sup>5,6</sup>. The temperature sensing

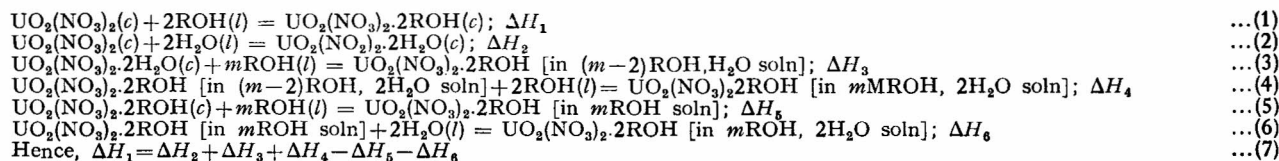
TABLE 1 — HEATS OF SOLUTION OF URANYL NITRATE DIHYDRATE AND URANYL NITRATE *bis*-ALCOHOL IN METHANOL AND ETHANOL AT 303°K

(Values in KJ mol $^{-1}$ )				
Compound	Weight (g)	Conc. M	$\Delta H_3$	$\Delta H_5$
SOLVENT: MeOH(l) (125 ml)				
$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}(c)$	0.94560	0.017592	-34.3	
	1.26285	0.023490	-34.3	
	1.27620	0.023740	-33.7	
			Av =	-34.4
				$\pm 0.2$
			2H O(c)	
EtOH (125 ml)				
$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}(c)$	0.48640	0.009048	-19.4	
	1.13830	0.021177	-19.4	
	1.59688	0.029708	-19.3	
			Av =	-19.4
				$\pm 0.1$
MeOH (125 ml)				
$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{CH}_3\text{OH}(c)$	0.54370	0.009496		-12.9
	0.78230	0.013664		-11.4
	0.86005	0.015022		-10.9
			Av =	-11.7
				$\pm 0.3$
EtOH (125 ml)				
$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{C}_2\text{H}_5\text{OH}(c)$	0.2725	0.004484		-16.4
	0.6838	0.011255		-15.2
	1.0589	0.018496		-15.8
			Av =	-15.8
				$\pm 0.5$

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.

Anhydrous uranyl nitrate is difficult to prepare. An indirect method<sup>7</sup> employing the following thermodynamic cycle has been used for the calculation of heats of reaction of  $\text{UO}_2(\text{NO}_3)_2(c)$  with alcohol,  $\text{ROH}(l)$ , to form  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{ROH}(c)$ .

In the above reactions,  $\Delta H_3$  and  $\Delta H_5$  have been determined experimentally and the values are listed in Table 1. For the heat of reaction of  $\text{UO}_2(\text{NO}_3)_2(c)$  with  $2\text{H}_2\text{O}(l)$  (Eq. 2), we have used the value<sup>8</sup>  $-58.6$  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  $\Delta H_4$  and has, therefore, been neglected. The heat of solution of water in excess of alcohol has



\*To whom all correspondence should be addressed.

been interpolated from the data<sup>8,9</sup> reported in the literature assuming that the presence of uranyl nitrate bis-alcohol will have no effect on the heat of solution.  $\Delta H_6$  thus estimated for methanol and ethanol complexes, respectively, are 0.42 and 1.5 KJ mol<sup>-1</sup>. Hence  $\Delta H$ , for  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{CH}_3\text{OH}(c)$  and  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{C}_2\text{H}_5\text{OH}(c)$  are  $-80.8$  and  $-60.6$  KJ mol<sup>-1</sup>, 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).

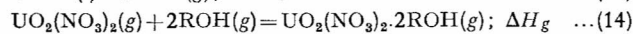
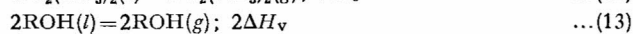
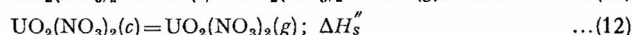
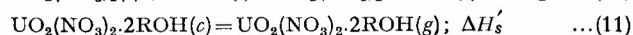
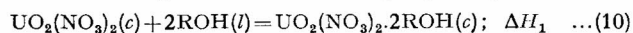
$$\Delta H_1 = \Sigma \Delta H_f^\circ (\text{products}) - \Sigma \Delta H_f^\circ (\text{reactants}) \quad \dots (8)$$

Therefore

$$\Delta H_f^\circ \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{ROH}(c) = \Delta H_f^\circ \text{UO}_2(\text{NO}_3)_2(c) + 2\Delta H_f^\circ \text{ROH}(l) + \Delta H \quad \dots (9)$$

By computing  $\Delta H_f^\circ \text{UO}_2(\text{NO}_3)_2(c)$  from Lange<sup>8</sup> and  $\Delta H_f^\circ \text{ROH}(l)$  from Cox and Pilcher<sup>10</sup>,  $\Delta H_f^\circ \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{CH}_3\text{OH}(c)$  and  $\Delta H_f^\circ \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{C}_2\text{H}_5\text{OH}(c)$  come out to be  $-1935.4$  and  $-1993.2$  KJ mol<sup>-1</sup>, respectively.

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



where  $\Delta H'_s$  and  $\Delta H''_s$  are the heats of sublimation of uranyl nitrate bis-alcohol and uranyl nitrate, respectively;  $\Delta H_v$ , the heat of vaporization of the alcohol; and  $\Delta H_g$  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<sup>6</sup> the heats of sublimation data are assumed to be the same for uranyl nitrate and the bis-complexes. Hence  $\Delta H_g$ , for the bis-methanol and bis-ethanol are  $-155.6$  and  $-145.8$  KJ mol<sup>-1</sup>; and the uranium-oxygen (alcohol) bond-strength,  $E(\text{O}-\text{U}) = -\Delta H_g/2 = 77.8$  and  $72.9$  KJ mol<sup>-1</sup>, respectively for methanol and ethanol adducts. The values compare well with the alcohol and  $\text{UCl}_4$  bond strength<sup>11</sup> in  $\text{UCl}_4 \cdot 4\text{ROH}$  and with the uranium-oxygen (water) bond strength reported earlier<sup>12,13</sup>. 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

N. C. DAS & P. B. DAS

Department of Chemistry, S.C.S. College, Puri

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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 equation. 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 ( $\phi$ ) 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<sup>1-11</sup>. 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  $< 0.1M$  at  $35^\circ \pm 0.001^\circ$ . 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<sup>12</sup>. The procedures for viscosity measurement were the same as described by Prasad *et al.*<sup>13</sup>. The density measurements were made by pycnometer (50 ml) with buoyancy correction and the values are accurate up to 4 in  $10^6$ . The concentration range was from 0.1 to 0.001M.

The applicability of the Jones-Dole equation<sup>2</sup> 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.