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Solvation enthalpy of uranium tetrachloride in aqueous-alcohols mixed solvents

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The process of interaction between ions of a solute and the molecules of the solvent through relatively weak covalent bonds is called solvation. It involves evening out a concentration gradient and evenly distributing the solute molecules within the solvent. Hydration is a special case of solvation when the solvent molecules are water. Solvation energy, generally, is the energy released when ions in crystal lattices associate with molecules in a solvent, however it can be positive or negative, depending upon the combined effects of lattice and hydration energies in case of aqueous-ionic solid dissolution. Uranous chloride or uranium tetrachloride (UCl_4) is a green crystalline solid which sublimes in vacuum at 500°C/10^{-3} mm. It is a Lewis acid and hence dissolves in solvents which can act as non-protic Lewis bases. Although dissolution of uranium tetrachloride crystals in water is an exothermic process yielding a green solution which is fairly stable in the cold, yet is hydrolyzed to a considerable extent to furnish an acidic reaction. Solvation enthalpies of quadrivalent uranium system have been scantly reported. The present communication deals with the calculation of enthalpy of solution of uranium tetrachloride in aqueous-non-aqueous solvent mixtures, particularly in 10 and 20 weight (wt) % methyl alcohol-water and ethyl alcohol-water systems at 25°C calorimetrically and thereby estimating the solvation enthalpy of UCl_4 in the said media.

Key words: Ethanol; methanol; exothermic reaction; solvation enthalpy; uranium tetrachloride.

Introduction

Uranium ($_{92}$U) which is one of the heaviest naturally occurring elements and which has six naturally occurring known isotopes ranging from U-233 to U-238 and is weakly radioactive, occurs naturally in varying but small amounts in soil, rocks, water, plants, animals, and in all human beings. In a typical sample of natural uranium, 99.27% of the mass consists of U-238 atoms, about 0.72% of the mass consists of U-235 atoms, and a very small amount of about 0.0055% by mass is that of U-234.[1] It is a silvery white metal and is malleable, ductile and slightly paramagnetic.

The heat or enthalpy of solution refers to the enthalpy change associated with the dissolution of a given amount of solute in a large excess volume of solvent at a given temperature and pressure, resulting in infinite dilution. It is generally expressed in kJ/mol. The enthalpy of solution of an ideal solution, by convention, is

taken to be naught. For non-ideal solutions of electrolytes it is connected to the activity coefficient of the solute(s) and the temperature derivative of the relative permittivity. On the other hand, solvation is a process of an interaction of a solute with the solvent molecules[2], leading to stabilization of the solute species in the solution. It involves evening out a concentration gradient and evenly distributing or dispersing the solute within the solvent via host of interactions. The enthalpies of solution, free energies and enthalpies of solvation are of fundamental importance since they constitute the basis of ion-solvent interactions.[3] For the most part, the Born equation (1) and the Born- Bjerrumequation (2) have dominated many attempts to calculate these quantities.[3]

$$\Delta G_{solv} = -\frac{(ze^2)}{2ri}\left\{1 - \frac{1}{\varepsilon}\right\} \tag{1}$$

$$\Delta H_{solv} = -\frac{(ze^2)}{2ri}\left\{1 - \frac{1}{\varepsilon} - \frac{T}{\varepsilon}\frac{\partial \ln \varepsilon}{\partial T}\right\}_P \tag{2}$$

where r_i is the crystal radii of the cations and anions and ε is the relative permittivity of the medium. Although various investigators have calculated enthalpy of solution and thereby other thermodynamic properties on that basis adopting various diverse methods, for example, Mark Salomon, in his paper, evaluated the energetics of single-ion solvation in water and propylene carbonate on the basis of electrostatic model.[3]

In this line, measurements of heat of solution of anhydrous uranium tetrachloride in aqueous HCl–LiCl mixtures at constant ionic strength were reported by Hearne and White[4]as early as 1957. Weeda and Somsen,[5] on the other hand, measured the enthalpies of solution of LiI, NaI, KF, KCl, KBr, KI, RbI and CsI in N-methylacetamide at 35° with the help of an adiabatic calorimeter and ionic enthalpies of solvation of the alkali metal and halide ions in N-methylformamide and N-methylacetamide were estimated. Solvation enthalpies of various nonelectrolytes in water, propylene carbonate,

and dimethyl sulfoxide were reported through the measurement of heats of solution of a number of nonelectrolytes mostly alcohols and hydrocarbons in the solvents like water, propylene carbonate, and dimethyl sulfoxide.[6] The enthalpy of formation of uranium tetrachloride, $UCl_4(s)$, in the absence of dissolved oxygen, was determined by Fitzgibbon et al.[7] from measurements of the enthalpies of solution of uranium metal and of $UCl_4(s)$ in 4 M and 6 M HCl containing added Na_2SiF_6. The heats of solution of the sodium n-alkyl sulphonates from methyl to octyl were evaluated at 25°C in water, D_2O, and three alcohol-rich mixtures with water, all at low solute concentrations so as to avoid solute-solute interaction completely.[8] Akabori et al.[9] determined the standard molar enthalpy of formation of UNCl from the measurement of enthalpy of solution of UNCl(s) and a mixture of UCl_4 and NH_4Cl in a mixture of HCl and $FeCl_3$ calorimetrically. The enthalpy of solution of trans-cyclohexyl-1,4-diamine and cis-cyclohexyl -1,2-diamine in water was determined calorimetrically.[10] Sedov et al.,[11] however, reported enthalpy of solvation of low polar solutes in formamide derivatives at 298 K. The heat of hydrolysis of uranium (IV) in perchloric acid solution was measured via spectrophotometric technique. A value of 10.7 ± 1 kcal per mole was obtained which was in good agreement with a previous value determined by a calorimetric method. The entropy of association of uranium (IV) with hydroxyl ion was found to be +52 e.u.[12] Previously enthalpies of precipitation of a number of oxinate complexes with divalent ions in aqueous phase have been studied and reported,[13]however, standard heats of formation of uranyl (II) and thorium (IV) oxinates have been computed by Thakur et al.[14] in later years. Some work had also been reported on uranium (VI) compounds earlier.[15,16] More recently thermochemical studies of thorium (IV) and zirconium (IV) tetrabenzoates have been reported by Pathak[17] but work on solvation enthalpies of quadrivalent uranium system have been very few and far between.

As solvation enthalpies of quadrivalent uranium system have scantly been reported, the

present paper deals with the calculation of enthalpy of solution of UCl_4 solution-calorimetrically in 10 and 20 weight (wt) % $MeOH–H_2O$ and $EtOH–H_2O$ systems at 25°C and thereby finding the solvation enthalpies of UCl_4 from the heat of solution data. Owing to the dearth of auxiliary thermodynamic data for polyvalent electrolytic system and complexity of the theoretical interpretations, the result have been discussed and can be considered as having mere data value.

Materials and Methods

Uranium being an active metal dissolves in dilute acids furnishing quadrivalent uranium, U (IV), which upon oxidation yields hexavalent uranium, U(VI), however, the two most common uranium species in aqueous solution being U^{4+} and UO^{2+}.[18] Uranium (IV) or (U^{4+}) ion which has a high charge density and smaller radius of 0.97Å or 97 picometre (pm), comparable to that of Na^+ ion (0.95 Å), has a strong polarizing power and in aqueous solution it hydrolyses as

$$U^{4+} + H_2O \rightarrow U(OH)_3^{3+} + H^+.$$

U^{4+} ions form stronger complexes with a given ligand. In presence of air or oxygen this aqueous solution turns yellow from green due to the formation of UO^{2+} ions.[19-21] The aforementioned reaction sans air does not take place. UCl_4 and its addition compounds are highly susceptible to hydrolysis and oxidation, consequently all manipulations were done in an atmosphere of dry nitrogen (N_2), devoid air and moisture completely. For this commercial nitrogen was purified by passing it successively through a tube containing Cu-turnings at 300-350°C to remove oxygen and then through tubes containing $CaCl_2$ + P_2O_5 and silica-gel to remove even traces of moisture.

Reagents of analytical grade were utilized for the preparation of crystalline compounds. UCl_4 was prepared by the action of hexachloropropene ($Cl_3C-ClC=CCl_2$ or HCP) on uranium trioxide (U_3O_8).[22] 20 gm of uranium trioxide was first dried at 110°C for several hours and then mixed with HCP (90 ml) and the mixture was heated in dry nitrogen-gas atmosphere. Since the reaction was brisk and highly exothermic in the beginning, it was necessary to cool the reaction mixture. When the reaction had subsided, the red coloured mixture was boiled under reflux for six hours, at the end of which the colour changed from red to green. The mixture was allowed to cool under nitrogen and the product was filtered. The residue containing UCl_4 was then washed several times with anhydrous carbon tetrachloride (CCl_4) to drive out the soluble impurities. The green crystalline UCl_4 so obtained was heated on a steam bath to remove CCl_4, if any. The crude sample of anhydrous UCl_4 (25 g; 90%) obtained as a green powder was stored under dry N_2 gas atmosphere. It was then purified through vacuum sublimation in a pyrex glass tube under the reduced pressure of $500°C/10^{-3}$ mm. The obtained UCl_4 solid was then analyzed for uranium and chlorine by the oxinate and silver chloride methods respectively[23] (Found: U, 62.5%; Cl, 37.0%; Calc. for UCl_4: U, 62.7%; Cl, 37.3%).

Reagent grade HCP was distilled from phosphorus pentoxide (P_2O_5) and middle fraction having boiling point (b.p.) 214°C was collected for use. Conductivity water was always used. Triply distilled ordinary distilled water with alkaline potassium permanganate ($KMnO_4$) collected in an all glass 'pyrex' glass receiver was used in all solvent mixtures.

Results

Results have been calibrated in Tables 1 to 4 which represent the enthalpies of solution of UCl_4 in 10 and 20 wt. % methanol-water systems and 10 and 20 wt. % ethanol-water systems respectively in complete absence of air under a dry nitrogen atmosphere to avoid oxidation and hydrolysis. In each case the compound dissolved instantaneously furnishing clear green solution which on protracted standing of about 24 hours in air exhibited the presence of a suspended colloidal precipitate which Young[24] identified it to be a hydrous oxide of U(VI). The heat of solution in aqueous HCl (1 mole of HCl per 8.808 moles of water had been found to be 39.4 ± 0.2 kcal $mole^{-1}$ (=164.85 ± 8.4 kJ $mole^{-1}$)[25] which compares well

Table 1 | Enthalpy of solution of UCl_4 crystal in 10 wt% $MeOH$-H_2O mixture at 25°C.
Molar mass of UCl_4 = 379.83 g mol^{-1}

$UCl_4(c)$		ΔH	$\Delta_{soln}H$
mg	m mole	J	kJ mol^{-1}
125.3	0.3298	84.2	- 255.3
132.8	0.3496	90.3	- 258.5
141.7	0.3730	96.0	- 257.4
151.6	0.3991	101.7	- 254.8
159.4	0.4196	107.5	- 256.2

Mean $\Delta_{soln}H$ = -256.4 ± 1.36 kJ mol^{-1}

Table 3 | Enthalpy of solution of UCl_4 crystal in 10 wt% $EtOH$-H_2O mixture at 25°C.

$UCl_4(c)$		ΔH	$\Delta_{soln}H$
mg	m mole	J	kJ mol^{-1}
91.3	0.2404	59.7	- 248.6
121.4	0.3196	78.5	- 245.8
136.2	0.3586	88.6	- 247.2
141.7	0.3730	93.0	- 249.4
145.2	0.3822	93.9	- 245.7

Mean $\Delta_{soln}H$ = -247.3 ± 1.48 kJ mol^{-1}

Table 5 | Solvation enthalpies of UCl_4 in aqueous-non-aqueous solvent mixture in kJ mol^{-1}.

	10 wt. %		20 wt. %	
Solvent	- $\Delta_{soln}H$	- $\Delta_{solv}H$	- $\Delta_{soln}H$	- $\Delta_{solv}H$
$MeOH$-H_2O	256.4	7833.9	274.5	7852.0
$EtOH$-H_2O	247.3	7824.8	266.8	7844.3

with the calculated values in tables 1 to 4 considering the fact that those have been calculated in 10 and 20 wt. % methanol-water systems and 10 and 20 wt. % ethanol-water mixtures.

Discussion

From the tables we find that the heats of solution data do not obey Debye-Huckel theory and the effects of concentration on the enthalpy of solution are not observed. Since the solution possesses very low concentration of the solute, it is presumed that the mean enthalpy of solution ΔH_S values are at infinite dilution ($\Delta_{soln}H^{\circ}$ or $\Delta_S H^{\circ}$). The enthalpies of solution when com-

Table 2 | Enthalpy of solution of UCl_4 crystal in 20 wt% $MeOH$-H_2O mixture at 25°C.

$UCl_4(c)$		ΔH	$\Delta_{soln}H$
mg	m mole	J	kJ mol^{-1}
81.2	0.2138	58.3	- 272.8
101.4	0.2669	73.4	- 275.2
109.8	0.2891	79.4	- 274.9
119.7	0.3151	86.2	- 273.6
137.4	0.3617	99.8	- 276.1

Mean $\Delta_{soln}H$ = -274.5 ± 1.17 kJ mol^{-1}

Table 4 | Enthalpy of solution of UCl_4 crystal in 20 wt% $etOH$-H_2O mixture at 25°C.

$UCl_4(c)$		ΔH	$\Delta_{soln}H$
mg	m mole	J	kJ mol^{-1}
71.4	0.1879	49.9	- 265.9
73.3	0.1929	51.8	- 268.5
75.4	0.1985	52.9	- 266.7
76.5	0.2014	53.9	- 267.8
77.2	0.2032	53.7	- 264.6

Mean $\Delta_{soln}H$ = -266.7 ± 1.38 kJ mol^{-1}

bined with the crystal energy of the UCl_4 give values for the solvation enthalpies of U^{4+}(solv) and the Cl^- (solv). The lattice energy (U_l) of UCl_4 (c) has been calculated from Kapustinskii equation (3)

$$U_L = K \cdot \frac{v \cdot |z^+| \cdot |z^-|}{r^+ + r^-} \cdot \left(1 - \frac{d}{r^+ + r^-}\right) \qquad (3)$$

where K= 1. 2025 × 10^{-4} J m mol^{-1}, d =3. 45 × 10^{-11} m, v = the number of ions in the empirical formula, r^+ and r^- = radii of the cation and anion respectively, and z^+ and z^- are the numbers of elementary charge on the cation and anion respectively,[26] taking ionic radii of U^{4+} and Cl^- ions as 97 pm and 181 pm respectively. The calculated value comes out to be –7577.5 kJ mol^{-1}. However, the theoretical value of lattice energy of UCl_4 (c) taking the same value of U^{4+} and Cl^- radiis found to be –7449.9 kJ mol^{-1}.[27] The difference between the two values happens to be – 127.6 kJ mol^{-1}, which is less than even 2%. Table 5 lists the solvation enthalpy values of UCl_4 in different solvent mixtures which has been calculated by applying the formulae,

$$\Delta_{solvn}H = U_L + \Delta_{soln}H$$

where U_L is the lattice energy of UCl_4 (c). It can be observed that the solvation enthalpies in different solvents are higher for 20 wt. % mixture than that for 10 wt. % mixture and they decrease in the order MeOH–H_2O > EtOH–H_2O. This can partially be explained based on steric phenomenon. As methyl alcohol is less bulky it will be accommodated around the small U^{4+} ion more favourably and conveniently than the ethyl alcohol.

Harned and Owen[28] have noticed that the interpretation of enthalpy of transfer of polyvalent electrolytes is rather complex and a number of interactions, mainly electrostatic and quantum mechanical play vital roles. However, it is for sure that from the enthalpies of solution data in aqueous and non-aqueous media, a host of thermodynamic properties, viz. enthalpy of solvation, enthalpy of vaporization, enthalpy of hydration, enthalpy of transfer, etc. can be calculated and results can be interpreted in various fruitful and tangible ways. In fact, Gill et al.[29] have calculated ΔC_p values, partial molar heat capacities for the solutes at infinite dilution, and even minimum solubility temperatures from the results of such data. Moreover, enthalpies of solvation data have been generously utilized by host workers to estimate the enthalpy due to solute-solvent interactions and for host of other thermodynamic purposes including the calculation of enthalpy for the formation of a cavity in a solvent using scaled particle theory (SPT).[30] From the tables 1-4, enthalpy of solvation of UCl_4 in 10 and 20 wt% in MeOH-H_2O and EtOH-H_2O mixtures has been calculated. Data of this type are very few and far between and therefore we reserve our discussion until more data are gathered in future.

The negative values of solvation enthalpies of UCl_4 (c) in 10 wt. and 20 wt. % methanol-water systems and 10 and 20 wt. % ethanol-water systems respectively clearly show the exothermicity of the reaction when UCl_4 (c) is dissolved in these mixture systems. Data of these types are very few and far between, and the present discussion would go a long way in stimulating research in the said field.

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