LASER RAMAN STUDIES OF THE STRUCTURE OF ELECTROLYTES IN AQUEOUS SOLUTIONS AND HYDRATED MELTS

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PREFACE

The study of structure of electrolytes in aqueous solutions and molten state has been and still is a subject of active interest. The interest in structural studies stems not only from fundamental curiosity but also from its usefulness in understanding various phenomena like diffusion,ionic mobility, supercooling and crystallization. The knowledge of the structural characteristics of the chemical species present in aqueous solutions and melts has, in fact, revolutionised the theory of electrolytic solutions and melts. The investigations on molten hydrated salts, which are simpler to study experimentally due to their low melting points, can help in understanding the role played by water in moderating the interionic interaction and hold a promise to bridge the gap between concentrated solutions and anhydrous melts.

The basic complication inherent in electrolytic solutions and melts is that these substances are representative members of the class of liquids, a state of matter whose microscopic structure has always been difficult to predict quantitatively from the known characteristics of the constituent molecules. In the liquid state one has appeal neither to the structural regularity of the crystalline solids nor

to the situation characteristic of dilute gases. In common with gases, ordinary liquids have an essentially disordered nature over distances in the substance of macroscopic size. The positions of neighbouring particles in liquids, and especially in concentrated aqueous solutions and melts, are often indicative of a strong, local ordering influence, or structure, which is a direct result of qualitative features of force laws acting between constituent atoms. The very nature of the liquid state precludes as detailed a description of the structure as one can obtain for gases or solids. In aqueous solutions and molten salts, specifications of detailed structure require more parameters than are ascertainable even by X-ray and neutron diffraction; these methods give only a modest description of the structure of liquids in terms of pair radial distribution function.

Amongst the wide variety of methods employed for these investigations, vibrational spectroscopy has since long been established as an effective technique. The vibrational spectra of the electrolytic solutions and melts can provide information about ion-ion interaction, ion-water interaction, geometry of polyatomic species and the nature of chemical bonds involved in the formation of these species. The vibrational frequencies can be measured by Raman effect and by infrared absorption. The strong absorption of infrared

radiation by water over wide regions of the spectrum, the lack of suitable water-insoluble optical materials, and difficulties of creating sufficiently short optical path-lengths alongwith the cost of operating in the far-infrared often discourage infrared studies of aqueous electrolytes. The transparency of water to visible radiation, the use of glass sample-containers and the capability of Raman spectrophotometer to provide useful information even down to 40 cm^{-1} have promoted the use of Raman spectroscopy for the study of aqueous electrolytes. Further, the development of laser sources having variety of frequencies, ranging from 632.8 mμ line of He-Ne laser to 484.0 mμ line of argon ion laser, allows one to select a suitable exciting frequency so that the colour of the sample is usually not a limiting factor. The polarization of the laser beam facilitates the measurement of depolarization ratios of Raman lines and this, in turn, provides valuable information about the structure of species present in a system.

In the present investigations, the author has employed Laser Raman spectroscopy to study certain electrolytes in the form of aqueous solutions and hydrated melts. Raman spectra in crystalline and glassy states of some of these electrolytes have also been investigated to facilitate the understanding of the structure of different types of

species present in the electrolytic solutions. The use of He-Ne laser as a Raman source has helped in the study of highly coloured aqueous solutions and hydrated melts of ferric salts.

The work reported in the thesis has been divided into seven chapters. In Chapter I, the basic concepts of Raman spectroscopy and its application to study the structural aspect of polyatomic molecules and ions have been briefly described.

Chapter II deals with the study of hydroxides of lithium, sodium and potassium in aqueous solutions. Prior to the present investigation, the Raman spectra of these hydroxides in aqueous solutions, mainly studied in the O-H stretching region, did not yield any information regarding interaction between OH^- and the metal ions; the spectra were complicated due to the presence of broad water bands. In the present work, the Raman spectra of these alkali metal hydroxides in aqueous solutions and also in methyl alcohol, over a wide range of concentration, in the low frequency region (50-600 cm^{-1}) have been studied. The detection of similar single, broad and weak low frequency bands (LFB's) in saturated KOH solutions, in water and methyl alcohol, and in saturated NaOH aqueous solution has clearly demonstrated

the presence of ion-pairs or clusters, involving some degree of electron sharing in the bond between K^+ or Na^+ and OH^- ions, in these solutions. The effect of dilution and increase in the temperature of the solution on these clusters have been studied. The absence of a similar LFB, even in saturated LiOH aqueous solutions, has been explained. The observed variation of refractive index with concentration and the earlier reported behaviour of electrical conductivity in NaOH, KOH and LiOH solutions have been discussed.

Chapter III is concerned with the structure of zincate and aluminate ions in concentrated alkali metal hydroxide aqueous solutions. A detailed analysis of Raman spectra of ZnO, $Zn(OH)_2$, Al_2O_3 and $Al(OH)_3$ in concentrated alkaline solutions has revealed that some of the low frequency bands, which were wrongly assigned to zincate and aluminate ions by the earlier workers, arise due to the presence of clusters formed due to the association between K^+ or Na^+ and OH^- ions. The identification of these clusters has contradicted the so far widely accepted tetrahedral model of zincate and aluminate ions. The present Raman evidence indicates that the most prominent species of zinc and aluminium in concentrated alkaline solutions exist as linear ZnO_2^{2-} and AlO_2^-.

Raman study of the structural characteristics of ferric perchlorate and nitrate in acidic solutions and of

crystalline $Fe(ClO_4)_3.9H_2O$ have been reported in Chapter IV. To avoid hydrolysis, acidic solutions of these salts have been preferred over the neutral solutions. No report on Raman investigation is available on hexa-aquoferrate complex ions which are known to be present in these solutions. In a recent Raman study on crystalline $Fe(ClO_4)_3.10H_2O$, it has been suggested that the Fe-O bond in hexa-aquoferrate complex is ionic. The present work has shown that the $Fe(H_2O)_6^{3+}$ species exist in acidic solutions of ferric perchlorate and nitrate and in crystalline $Fe(ClO_4)_3.9H_2O$. The Fe-O bonds in this complex have been found to be covalent.

In contradiction to earlier absorption spectroscopic report, no Fe^{3+}-ClO_4^- ion-pairs have been detected in acidic ferric perchlorate solutions. In the case of crystalline $Fe(ClO_4)_3.9H_2O$, the present Raman study supports the result of earlier infrared investigation which has revealed the presence of simple ionic ClO_4^- ions in the salt. In highly acidic ferric nitrate solutions, the evidence obtained indicates the presence of Fe^{3+}-ONO_2^- ion-pairs which involve sufficient degree of electron share in the Fe-O bond.

A detailed analysis of Raman spectra of crystalline, molten and glassy states of ferric chloride hexahydrate and ferric chloride hexadeutrate has been described in Chapter V.

Earlier to this work, Raman investigation has been reported very recently only on crystalline ferric chloride hexahydrate (FCHH). The present results reveal that different types of species are present in different states of the material. In the case of crystalline FCHH, the results are in agreement with those of X-ray diffraction and an earlier Raman investigation. Except for the disparities in the relative intensities of three bands, Raman spectrum of crystalline ferric chloride hexadeutrate (FCHD) has been found to be similar to that of crystalline FCHH. In view of this similarity, it has been proposed that the crystalline FCHH and FCHD are isomorphous, although some expansion of the lattice in the case of FCHD is probable.

The only available absorption spectroscopic report on molten FCHH has indicated that $FeCl_4^-$ ion, alongwith a small concentration of octahedral species of ferric ion, exists as the most prominent species. The present Raman investigation on molten FCHH and FCHD has confirmed that the $FeCl_4^-$ ion is the most prominent species and the structure of the octahedral complex has been found to be trans $Fe(H_2O)_4Cl_2^+$ and trans $Fe(D_2O)_4Cl_2^+$ in the respective melts.

It has been found, in agreement with the available Mössbauer spectroscopic study on glassy FCHH, that the ferrate

species in the glassy FCHH and FCHD are present in octahedral coordination. The probable structure of the species, which are present in a polymeric form, has been proposed. The processes of crystallization and glass formation have also been discussed.

Chapter VI deals mainly with the structure of ferric chloride hexahydrate (FCHH) in acidic and neutral aqueous solutions. Earlier X-ray and absorption spectroscopic reports on the structure of ferric species present in these solutions are rather controversial and conflicting. The present Raman investigation, carried out for the first time, has helped in a better understanding of structure of various species present in acidic and neutral solutions. In brief, the species present in these systems can be divided into three main categories viz. tetra-chloroferrate ion ~~ion~~, polymeric species and lower chloro-aquoferrate complexes. The relative concentrations of various species in a ferric chloride aqueous system have been found to vary with the concentration of ferric chloride and the acidity of the solution. The structure of polymeric species, which shows characteristics similar to that of the polymeric species present in glassy FCHH, has been discussed.

Raman study of ferric nitrate in crystalline

hydrate - $Fe(NO_3)_3.9H_2O$ - and in liquids of composition $Fe(NO_3)_3.XH_2O$, where X varies from 9 to 58, forms the last chapter of this thesis. To the best knowledge of the author, no report on detailed Raman investigation of ferric nitrate in variably hydrated liquids or on crystalline hydrate has appeared so far. The present investigation has indicated that NO_3^- ions and $Fe(H_2O)_6^{3+}$ ions exist in two distinct environments in the unit cell of monoclinic $Fe(NO_3)_3.9H_2O$ crystal. In molten $Fe(NO_3)_3.9H_2O$, the evidence has shown the presence of a nitrate complex, formed due to the association of NO_3^- ions in monodentate fashion with Fe^{3+} ions and containing a few water molecules. The effect of increase in the water content of the melt on the nitrate complex has been discussed. The presence of hydrolysis product in $Fe(NO_3)_3.XH_2O$ systems, ($X \geq 28$), has been detected. The various results obtained, also, throw more light on the observed large supercooling in the $Fe(NO_3)_3.9H_2O$ melt.

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