Abstract

Mixed systems made from a combination of ferroelectric (FE) and antiferroelectric (AFE) compounds, exhibit various effects of disorder in different temperature regions. The kind of effects observed, depend on the technique and the window of observation employed. Model systems, like Potassium Ammonium dihydrogen phosphate (KADP), Rubidium Ammonium dihydrogen phosphate (RADP) and BPxBPI(1-x) , with H-bonding networks, have been well studied by dielectric techniques. These investigations have revealed disorder effects like deviations from Curie Weiss law, progressive broadening of dielectric loss curves and dispersion of dielectric constant, at sufficiently low temperatures. NMR studies in such systems are meager and mainly members of the KDP family, like Rubidium ammonium dihydrogen phosphate (RADP) and arsenate (RADA) have been investigated using mainly 2H and 87Rb NMR. On the other hand, proton NMR has been much less used, and our focus is to exploit its power/potential to study 1H group dynamics in the presence (and absence) of disorder in condensed matter systems.

This thesis describes the results of proton NMR investigations in two mixed systems of ferroelectric and antiferroelectric compounds namely, (i) Betaine phosphate (BP, AFE) and Betaine phosphite (BPI, FE) and (ii) Betaine phosphate and Glycine phosphite (GPI, FE). The aim of the study is to obtain information on 1H group dynamics (activation energies and pre-exponential factors) and the effects of micro-spatial disorder. The former system is shown to exhibit orientational glass behavior by extensive dielectric investigations. BP-GPI system is synthesized for the first time and our proton NMR investigation has exhibited interesting effects of disorder like deviation from expected BPP behavior. Further, both systems have exhibited quantum tunneling effects, revealing a gradual transition from classical regime to quantum regime. Biexponential magnetization recovery at low temperatures has also been observed indicating the existence of disorder.

A combination of AFE and FE compounds of this type form a mixed system, over a broad range of compositions, in which the long-range electric order is suppressed owing to frustration effects. Such systems have been treated as dipolar analogues of spin glasses and are known as ‘orientation glasses’ (OG), ‘proton glasses’ (PG) or ‘pseudo-spin glasses. Although the frustrated condensed matter system is crystalline in nature, there is an underlying microstructural randomness due to local fluctuations of the composition which usually results in static lattice strains, which are called random fields. It has been shown that these random fields can also have a pronounced effect on the spin lattice relaxation time as observed in NMR experiments. Depending on the relative concentration and temperature, the mixed system exhibits a range of states (x-T phase diagram) like FE, OG, coexisting OG and AFE, and AFE.

These mixed systems exhibit various kinds of effects of disorder in different temperature regimes which depend upon the technique and window of observation. For e.g., using dielectric spectroscopy we can study the behavior of the electric dipoles during various phases and the effects of frustration seen as dispersion of dielectric constants and broadening of loss curves etc. Through quadrupole perturbed NMR study of systems containing nuclei like 87Rb or 2H, we learn about site-specific inhomogeneities and distribution of EFG in the system. Proton NMR study in the mixed systems, though not much used so far, is a powerful technique to shed light on the dynamics, disorder and Quantum tunneling effects.
Our proton SLR time measurements have been carried out at two Larmor frequencies of 23.3 MHz and 11.4 MHz, in the temperature range of 300 K to 4 K and the results are presented in this thesis, which is divided into four chapters.

The relevant basics of the NMR are described briefly in Chapter 1. Brief description of the important aspects relevant to the present studies like dipole-dipole interaction, spin-lattice, spin spin interaction, spin diffusion, quantum rotational tunneling etc., are given.

The pulsed NMR spectrometer used in the present experiments is described in Chapter 2. A versatile programmable pulse generator has been designed and fabricated by the author and described in detail. All the subsystems like the magnet power supply, mixer, transmitter, and receiver as well as the RF probe have been reconditioned/rebuilt to achieve good performance. The sample temperature has been varied using a continuous gas flow Helium cryostat (CF200 Oxford Instruments) and the temperature is controlled to an accuracy of ± 0.5 K, with the aid of ITC4 temperature controller. The operation of the spectrometer and experimental method of data collection is also described.

In Chapter 3, the NMR studies in BP, BPI and BPxBPI(1-x) are described. The first part presents an introduction to the mixed system along with a brief review of the literature, covering different techniques like XRD, dielectric, ultrasonic, ENDOR, NMR, IR, Raman, conductivity, and specific heat studies. All these investigations are seen to focus only on the O–H···O dipoles and their frustration effects on the system.

In the second part, comprising of the present investigation, preparation of the samples of BP, BPI and BPxBPI(1-x) for x = 0.25, 0.45 and 0.85 is described followed by characterization of the samples by XRD and IR studies. This is followed by a detailed presentation of the experimental results of each sample and the analysis of the T1 Vs 1000/T results in the temperature range 300 K to 4 K at 23.3 MHz and 11.4 MHz. The high temperature region (300 K - 100 K) and the low temperature region (100 K - 4 K) results are described separately, as different models are used for their analysis. The results display different features like the BPP type relaxation (and also deviations from it) and quantum tunneling assisted relaxation.

The spin lattice relaxation time (T1) data of the parent compounds BP and BPI in the high temperature region has been analyzed using a modified BPP equation and show the expected characteristics (like parallel slopes on the low temperature side of T1 minimum and Larmor frequency scalability). In the low temperature region, the T1 data has been analyzed on the basis of Lourens' methodology which considers the presence of a number of sub ensembles of CH3 or NH3 groups with distributed activation energies causing T1 minima at successive temperatures, showing a gradual transition from classical reorientation to tunneling rotation. Some of these results have been published in **[1] phys. stat. sol. (b). 2006; 243(8): 1929-1938.**

The T1 data in the mixed system BPxBPI(1-x) at the two Larmor frequencies in the higher temperature region (300 K - 100 K) is analyzed by a modified BPP equation which gives the effective relaxation rate in the mixed system as a superposed sum of two BPP type equations, one each for BP and BPI, weighted by their relative concentrations.

These results also reveal the presence of disorder effects at a relatively higher temperature (~170 K) revealing the presence of sub ensembles of methyl groups with different activation energies. The trimethyl group reorientation gives rise to a T1 minimum at a higher temperature but shows less changes of activation energy with Larmor frequency or concentration. Some of these results have been published in **[2]Mol. Phys. 2006; 104(20-21): 3213-3223.**

The T1 data in the low temperature range (100 K – 4 K) has shown a weakly temperature dependent relaxation, which has been analyzed by Lourens method. The low temperature data has shown concentration dependent features like exponential and biexponential magnetization recovery, and disappearance of relaxation in different temperature intervals, and gradual transition from classical to quantum regime.

The salient features observed observed are: (i) normal BPP behavior in the parent compounds; (ii) Deviation from the BPP model in the mixed systems; (iii) Non-parallel slopes on the low temperature side of the methyl T1 minimum; (iv) Distribution of activation energies and tunnel level energy difference; (v) biexponential magnetization recovery below 50 K; (vi) Disappearance of NMR signal in different temperature intervals in the different compositions, etc.

In Chapter 4, proton SLR investigation of disorder in the mixed system BPxGPI(1-x) is described in part I. This mixed system is new and has been synthesized for the first time, using BP (AFE) and GPI (FE). Earlier work in GPI using XRD, dielectric, IR and NMR techniques from literature has also been briefly described.

In part II, comprising of the present investigation, preparation of samples of BP, GPI, and BPxGPI(1-x) for x = 0.8, 0.7, 0.6, 0.5, 0.4 and 0.3 and characterization by powder XRD and IR techniques are described. The XRD (Intensity Vs 2θ) data was analyzed by Proszki, a powder XRD analysis software and refined by iteration and the lattice parameters have been determined. The IR absorption data of the mixed system has been compared with that of the parent compounds.

The proton SLR T1 measurements and results at 23.3 MHz and 11.4 MHz in the temperature range between 300 K and 4 K for all compositions are presented in two sections (i) from 300 K to 100 K and (ii) from 100 K to 4 K. A model for the effective relaxation rate has been developed on the same lines as done in BPxBPI(1-x) to analyses the T1 data of the classical region in the mixed system. The low temperature T1 data (< 100 K) has been analyzed on the basis of Lourens' model.

The salient features observed in these systems are; (i) The slopes on the low temperature side of the classical minimum at the two Larmor frequencies in the mixed system are not parallel but are inclined to each other at various inclinations and in some cases cross each other as a function of concentration, which is explained in terms of CH3 groups having a distribution of Ea values; (ii) A gradual transition from classical motions to quantum tunneling rotation of methyl groups; (iii) A distribution in the activation energy Ea and E01 (the difference between the ground and the first excited energy levels of the torsional oscillator states of methyl rotors) below 100 K; (iv) The magnetization recovery of protons is exponential above 50 K and biexponential below 50 K in some concentrations, except for x = 0.3 and 0.4, where the magnetization recovery becomes biexponential at 180 K itself; (v) the FID signal disappears and reappears in different ranges of temperature depending upon 'x'. **Some of these results in BPxGPI(1-x) have been published in** M.N.Ramanuja et al,Magn. Reason. Chem. **45**(12), 1027-1034, (2007).