
^{35}Cl NQR Study of Cation Polarizability in Metal Salts of Monochloro Acetic Acid

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Various metal salts (Na, K, Rb, and NH_4) of monochloro acetic acid were prepared and the ^{35}Cl nuclear quadrupole resonance frequencies were measured at room temperature. A comparative study of nuclear quadrupole resonance frequencies of monochloro acetic acid and its metal salts is carried out. The frequency shifts obtained in the respective metal chloroacetates are used to estimate the changes in the ionicity of C–Cl bond. Further, the changes in the ionicity of C–Cl bond were used to estimate the percentage of intra-molecular charge transfer between respective cation–anion of the metal salts of chloro acetic acid. The nuclear quadrupole resonance frequency is found to decrease with increasing ionicity of the alkali metal ion.

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1. Introduction

The aim of the present work is to find a correlation between the ^{35}Cl nuclear quadrupole resonance (NQR) frequency and the cation polarizability. Various crystalline metal salts of monochloro acetic acid of general formula, $\text{CH}_2\text{ClCOO}^- \text{M}^+$ ($\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{NH}_4$) are obtained by the replacement of hydrogen atom in the chloro acetic acid by metal ions such as sodium/potassium/rubidium and ammonium. They form a large class of ionic crystals exhibiting new and interesting

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physical as well as chemical properties. Study of solid metal chloroacetates is of great importance. They find use as precursors to produce respective polyglycolide and metal halide [1]. The elimination of metal halide from the reaction products gives rise to respective polyglycolide. More recently, there is large scope for the use of polyglycolide product in a variety of material applications. These polyglycolides are nontoxic, easily bio-degradable, possess highly porous structure, and use inexpensive precursor compounds. A more specialized application of polyglycolides is in the field of medical technology as implants within the human body. Typical applications are as carriers for controlled drug release and bio-materials [2].

These metal chloroacetates have been thoroughly characterized using various spectroscopic methods, namely NMR, IR and scanning electron spectroscopy. In addition, thermoanalytical techniques such as differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) are also employed [3]. Elemental analysis and X-ray powder diffraction (XRD) have supplemented these investigations [4]. However, the question as to how metal ions and halogen ions find themselves to form the metal halide lattice along with respective polyglycolide is still not completely resolved [2].

NQR spectroscopic method has been used for chemical structure analysis of various types of molecular compounds. It provides a fairly sensitive probe of the local electrical environment of the quadrupolar nuclei. The first result of ^{35}Cl NQR investigation on the solid monochloro acetic acid and substituted monochloro acetic acid was reported by Allen in 1952 [5]. Beidenkapp and Weiss [6] have measured the chlorine quadrupole resonance frequency of metal salts of trichloro acetic acid. A study is carried out to investigate the hydrogen bond structure in a wide range of acid chlorocarboxylate salts by the NQR method [7]. A detailed NQR study of ammonium hydrogen and deuterium bis monochloroacetates has also been reported [8]. Study on the Zeeman NQR spectra of monochloroacetic acid has revealed the asymmetry parameter to be ≈ 0.02 for both chlorine sites of monochloro acetic acid whereas it was not possible to observe Zeeman splitting in the case of sodium chloroacetate. It was concluded that true covalent character of C–Cl bond is about 1% [9]. It follows that solid chloroacetic acid is primarily ionic with a considerable amount of polarization of each ion.

As the studies on metal salts of monochloro acetic acid is quite significant, ^{35}Cl NQR frequency data have been used to evaluate the chemical bond parameters, namely double bond character and the ionicity of the C–Cl bond. Further, the difference in the ionicity of C–Cl bond of metal chloroacetates with that of monochloro acetic is used to estimate the percentage of intra-molecular charge transfer between respective cation–anion of the metal salt of monochloro acetic acid.

2. Results and discussion

The experimentally observed ^{35}Cl NQR frequencies of chloro acetic acid and the respective metal chloroacetates are shown in Table I along with their melting

points. A single resonance line has been observed at room temperature in all metal chloroacetates which confirms chemical equivalence of chlorines [10]. Moreover, the observed frequency shifts in comparison to monochloro acetic acid are in the range 1.2 MHz to 2.2 MHz which cannot be attributed to the crystalline field effects. It is well known that crystalline field effects generally lead to the frequency shifts of the order of ± 200 kHz [11].

TABLE I

³⁵Cl NQR frequencies, frequency shifts and melting points (M.P.).

Compound	M.P. [$^{\circ}$ C] (decomp. temp.)	Resonance frequency at 300 K [MHz]	Frequency shift [MHz]
1. Chloro acetic acid (α -phase)	62	34.904, 35.406 (av.) 35.16	–
2. Sodium chloroacetate	197	33.91	–1.25
3. Potassium chloroacetate	156	33.29	–1.86
4. Rubidium chloroacetate	122	33.01	–2.15
5. Ammonium chloroacetate	105	33.21	–1.94

The NQR frequency of chlorine depends strongly on the ionicity of C–Cl bond and may be used to measure the chemical bond parameters such as ionic character and double bond character of C–Cl bond in crystalline materials [12]. Townes and Dailey theory has been used to relate NQR frequency to the ionicity of the C–Cl bond [13]:

$$\frac{e^2 Q q_{\text{mol}}}{e^2 Q q_{\text{atom}}} = \frac{\nu_{\text{mol}}}{\nu_{\text{atom}}} = 1 - S^2 - I - \pi, \quad (1)$$

where Q is the quadrupole moment, q is the maximum electric field gradient, ν is the NQR frequency, S^2 represents s -hybridization, I is the ionicity, π is the double bond character. Das and Hahn [14] have reported the ν -value for atomic chlorine as 54.873 MHz. Using this with Eq. (2) representing Bersohn relation [15], the double bond character π can be estimated. Knowing the value of S^2 and π in Eq. (1), the ionicity I can be calculated.

$$\pi = \frac{2\eta}{3(1+C)} \left(\frac{\nu_{\text{mol}}}{\nu_{\text{atom}}} \right), \quad (2)$$

where η is the asymmetry parameter of the electric field gradient for C–Cl bond, taken from the earlier report [9] and the correction factor, $C = 0.15$.

2.1. Percentage of charge transfer

The estimated ionicity (I) and double bond character (π) in the C–Cl bond for the metal salts of monochloro acetic acid are shown in Table II. It can be seen that the ionicity of C–Cl bond seems to vary with the intra-molecular charge

transfer in metal chloro acetates. The difference in ionicity of C–Cl bond with reference to monochloro acetic acid is used to estimate percentage of charge transfer between cation–anion of metal chloroacetate. The values are shown in Table II.

TABLE II
Chemical bond parameters of C–Cl bond and % of charge transfer.

Compound	π [%]	I [%]	Intra-molecular charge transfer [%]
1. Chloro acetic acid (α -phase)	0.74	20.2	–
2. Sodium chloroacetate	0.71	22.5	10.2
3. Potassium chloroacetate	0.70	23.6	14.4
4. Rubidium chloroacetate	0.69	24.2	16.5
5. Ammonium chloroacetate	0.70	23.8	15.1

The frequency data in the compounds studied indicate the cation influence on the chloroacetate anion increasing in the order -Na, -K, -NH₄, -Rb. The observed NQR frequency shift in these compounds are due to charge transfer induced by polarization of the alkali metal. The following arguments justify the observation.

The metal chloroacetates have strong cation–anion interaction giving rise to stable, ionic crystals of general formula CH₂ClCOO[–]M⁺ (M = Na, K, Rb, NH₄). The electric field gradient at the chlorine nucleus arises from the electrons in C–Cl bond and the cation contributes significantly to the field gradient. This is through the charge density of the neighboring carboxylate oxygen atoms. The oxygen charge density can influence the electric field gradient by direct “through space” effect on the Cl atom and an indirect “polarization effect” on the C–Cl bond [16].

Fuentealba and Reyas [17] have calculated the electrostatic dipole polarizability α_y for the alkali-metal atoms in the ground state. Also, studies have revealed that the Sternheimer antishielding factor [18, 19] for alkali metals varies linearly from sodium to rubidium. A comparative examination of the quadrupole coupling constant of the alkali-metal halides, investigated in the gaseous phase by the microwave and molecular beam methods, shows that alkali halides are purely ionic compounds. The electric field gradient on the nuclei of the ions are calculated from the electrostatic model [20]:

$$eq_x = \pm \frac{2}{R^3}(1 - r_\infty) \left(1 + \frac{3\alpha_y}{R^3} \right). \quad (3)$$

The positive sign refers to halogen nuclei and negative to alkali, α_y is the dipole polarizability of the other ion and R is the distance metal–halogen. A linear dependence of e^2Qq_x on R^{-3} is observed for most alkali halides. Both, Sternheimer antishielding factor (γ_∞) and dipole polarizability (α_y) have influence on the electric field gradient of the halogen and vice versa. Hence, the observed shift in frequency in the metal chloroacetates can be explained.

It is clear from Table III that the dipole polarizability including core polarization potential (α_y) increases as the size of alkali ion increases. As the core electrons are more numerous in rubidium, it tends to have a higher polarizability and thus the density of electron cloud increases at the C–Cl bond as one moves from sodium to rubidium. Hence the sodium salt has a higher NQR frequency compared to the rubidium salt indicating that rubidium salt is more ionic. Also, the ammonium (NH_4) radical form a stable group identical to the alkali metal like sodium as it has eight inner shell electrons [8]. Hence the observed NQR frequency shifts and increase in ionicity of C–Cl bond are directly associated with the *core electron polarization*.

TABLE III
Dipole polarizability and the Sternheimer antishielding factor for alkali metals.

Alkali metals	Dipole polarizability (α) [\AA]	Sternheimer antishielding factor (γ_∞)
sodium	162	–4.53
potassium	290	– 12.8
rubidium	320	–70.7

The modifications introduced by the nature of the cation leads to an increase in ionicity of C–Cl bond as well as a significant NQR frequency shift in the respective metal chloroacetates in comparison with the monochloro acetic acid. Moreover, the relative displacement between the anion and the respective cation can add to the polarization effects and hence the observed charge transfer. Thus, NQR resonance frequencies of metal chloroacetates are varying with the charge of the cation. From these observations, it appears that the results obtained in the present study are in agreement with the theoretical considerations.

2.2. Conclusion

The replacement of hydrogen ion by the metal cations in monochloro acetic acid appears to increase the ionic character of the metal salts and hence a corresponding decrease in ³⁵Cl NQR frequency. The interaction between the metal cation and the chloro acetate anion induces the charge transfer process in these ionic crystalline materials. The analysis of results obtained in the present work indicate that besides intra-molecular charge transfer, the effects like induced polarization, exchange repulsion, geometric structure of the compounds make significant contribution to the charge rearrangement produced by the metal cations. The present analysis of NQR results and X-ray data appears to imply that chlorine atom in the metal salt of chloroacetic acid is bonding with the cation of the

neighboring molecule at the decomposition temperature of the compound giving rise to respective metal halide (M-Cl) and polyglycolide ($-\text{CH}_2\text{COO}-$)_n.

3. Experimental

3.1. Materials and preparation

All four metal chloro acetates used in the present investigation are prepared in the laboratory. The starting chemicals used in the present work are acetic acid, alkali metal hydroxides, ethyl alcohol, concentrated aqueous solution of ammonia.

Sodium, potassium and rubidium chloro acetates are prepared by neutralizing a concentrated solution of monochloro acetic acid in ethyl alcohol with equimolar amount of the corresponding alkali metal hydroxide in ethyl alcohol at room temperature. The water and excess solvent are removed in a rotary evaporator. The residue obtained is recrystallized from ethyl alcohol and dried in vacuum. Ammonium chloroacetate is prepared by adding a concentrated ethanolic solution of chloroacetic acid to an excess of a concentrated aqueous solution of ammonia. Water and ethanol are removed in a rotary evaporator. The residue thus obtained is recrystallized from ethyl alcohol. Generally, all compounds crystallize as very thin platelets or needles. The compounds are characterized by powder XRD, elemental analysis, melting point and the results match very well with those reported earlier [2].

3.2. Measurement of NQR frequency

The NQR frequencies of these compounds are observed using a home-made frequency modulated, self quenched, super regenerative oscillator (SRO) of Dean's type coupled with a lock-in amplifier and strip chart recorder [21]. NQR resonance signals of metal chloroacetates are weak in comparison with that of monochloro acetic acid. Hence, recording was preferred for identification and measurement. The signal-to-noise ratio was in the range 2–4. The NQR frequencies are measured by the standard beat method with an accuracy of ± 1 kHz.

Resonance frequencies measured at around room temperature (300 K) are in agreement with those reported earlier [7]. A finite frequency shift in the ^{35}Cl NQR frequencies of different metal chloroacetates in comparison with the mono chloroacetic acid, confirms the structural changes. The thermal stability of these salts are tested by heating them to a temperature of 320 K and cooling to 288 K. The observed ^{35}Cl NQR frequency remain unaltered at room temperature (300 K) ensuring the thermal stability.

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