# $^{36}$Cl-NMR Parameters for Molten Salt Reprocessing Analyses: Quadrupole Moment, Spin-Lattice Relaxation and Sternheimer Antishielding Factor for Chloride and Perchlorate Ions.

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# $^{36}$Cl-NMR Parameters for Molten Salt Reprocessing Analyses: Quadrupole Moment, Spin-Lattice Relaxation and Sternheimer Antishielding Factor for Chloride and Perchlorate Ions

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$^{36}$Cl is one of long-lived β-active isotopes with a half-life of $3 \cdot 10^5$ years and rare nuclear structure – its odd-odd nuclei contain 19 neutrons and 17 protons. Being an artificial isotope, $^{36}$Cl is not today an environmental hazard because of its low abundance. However, some of the scenarios for the development of atomic power, p.e. involving the use of molten chloride reactor systems for destruction of weapons plutonium and pyrochemical reprocessing of spent nuclear fuel, may result in accumulation of $^{36}$Cl due to $^{35}$Cl(n,γ)$^{36}$Cl reaction ($\sigma$ = 100 barn) in amounts that cannot be ignored as radioactive waste. Either U and Pu nuclear fission in molten reactor or Na(α,n)Al ($\sigma$ = 50 mbarn) at the fuel reprocessing step, could be the sources of neutrons to provide with such an accumulation of $^{36}$Cl. Thus, methods for analytical control of $^{36}$Cl will be required, $^{36}$Cl-NMR being one of the candidates.

Nuclear characteristics of the isotope $^{36}$Cl were reported in [1]: $I = 2$, $\mu = 1.31$ μB, electric quadrupole moment $Q$ = - 0.017 barn. In [2] $^{36}$Cl magnetic moment $\mu(^{36}\mathrm{Cl})$ = 1.2838 nm was determined from the ratio of the resonance frequencies $\nu(^{36}\mathrm{Cl})/\nu(^{2}\mathrm{H}) = 0.74873 \pm 3$. The magnetic moment was assigned the positive sign. In [3], the T dependence (260-330 K) of the spin-lattice relaxation time $T_1(^{36}\mathrm{Cl})$ of the $ClO_4^-$ ion in 64% perchloric acid, with less than 5% $^{36}$Cl, was measured, $T_1(^{36}\mathrm{Cl})$ in the $ClO_4^-$ ion being one order of magnitude greater than $T_1(^{35}\mathrm{Cl})$ and $T_1(^{37}\mathrm{Cl})$ in an aqueous $NaClO_4$ (1.2 M). Here, we report the results of comparative study of the spin-lattice relaxation times and $^{35}$Cl, $^{36}$Cl, and $^{37}$Cl NMR spectra of $Cl^-$ and $ClO_4^-$ ions in the solid state and solutions. The major objective of the work was (i) to determine the electric quadrupole moment of the $^{36}$Cl isotope by NMR and (ii) to estimate the Sternheimer antishielding factor γ for the perchlorate ion in terms of the Hertz spin-lattice relaxation theory.

## EXPERIMENTAL

The initial 30% HCl containing ca. 0.4% $^{36}$Cl was reacted with KOH to produce an alkaline solution of KCl, which was subjected to electrolysis (current density on a platinum electrode was 0.2 A/cm$^2$) in the presence of the catalyst $K_2CrO_4$ at 70$^o$C for several days, followed with the electrolysis at 10—15$^o$C and 0.8 A/cm$^2$.[1] The resulting sample was a solution of KCl and $KClO_4$ mixture, which was 0.1 M in the overall salt (sample 1). A portion of it was exhaustively electrolyzed to produce $KClO_4$, followed by the reaction with $Bu_4NOH$. The isolated solid salt $Bu_4NClO_4$ was used to prepare a 3.3 M solution in acetonitrile (sample 2). The solid anhydrous $Bu_4NClO_4$ was also studied (sample 3). The isotope contents of the samples were determined by mass spectrometry of the solid salt $Bu_4NClO_4$ pressed into a bismuth target.[2] The isotope composition of the salt found by mass spectrometry: $^{35}$Cl : $^{36}$Cl : $^{37}$Cl = 75.08 : 0.28 : 24.64. The independent determination of the $^{36}$Cl content by measuring the specific β-activity of $Bu_4NClO_4$ by liquid scintillation counting in 'Ready-Gel' cocktail on Beckman 6500 LS gave the $^{36}$Cl abundance of 0.4 wt-Cl %.

Spin-lattice relaxation times ($T_1$) and NMR spectra for three chlorine nuclides were measured on Bruker AC-200 and MSL-300 FT radiospectrometers at 300.0 ± 0.1 and 292 ± 2 K, respectively. The resonance frequencies and nuclear characteristics of the isotopes are listed in Table 1. Spin-lattice relaxation times $T_1$ were measured with the use of the inversion-recovery pulse sequence, $(180^o - \tau - 90^o)$-$5T_1$. The 90$^o$ pulse width was determined based on the greatest signal intensity and constituted 14 (12), 12 (11.2), and 15 (13) μs for $^{35}$Cl, $^{36}$Cl, and $^{37}$Cl, respectively, at resonance frequencies corresponding to the field of 7.042 T (4.6975 T). At a field of 7.042 T, free induction decays in $T_1$ measurement were accumulated in 8K memories. The spectral width was 1 kHz. In each of $T_1$ experiments, 12 to 14 time delays $\tau$ were specified. The number of transients accumulated was 100 for $^{36}$Cl and 10 for $^{35}$Cl and $^{37}$Cl. NMR spectra were recorded using one-pulse excitation with a varied dead time. At a field of 4.6975 T, experiments were carried out at 300 K with both external and internal deuterium locks. Spectral widths of 100 to 500 Hz were employed with 8K to 32K data points.

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[1] The synthesis of perchlorates has been described in Karyakin, Yu.V. and Angelov, I.I., Chistye khimicheskie veshchestva (Pure Chemical Compounds), Moscow: Khimiya, 1974

[2] We thank A.S. Alikhanyan for isotope mass spectral analysis

Specified temperatures were maintained constant by means of a VT-1-1000 temperature-control unit. Chemical shifts were referenced to a saturated aqueous NaCl solution.

## RESULTS AND DISCUSSION

The $^{35,36,37}$Cl NMR spectra of sample 1(Fig.1) showed two lines that arose from hydrated $ClO_4^-$ and $Cl^-$ ions. The integrated intensity ratio for these signals was $I[ClO_4]/I[Cl] = 1.43 \pm 0.08$. Since the chemical shift between $ClO_4^-$ and $Cl^-$ is 1002 ppm, each of the signals was recorded separately under different spectral conditions.

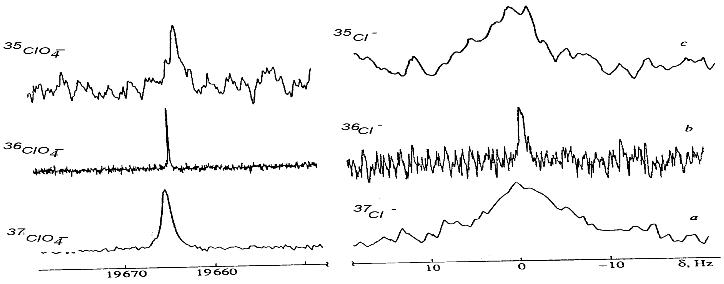

**Fig. 1.** NMR spectra (B = 4.6975 T) of an aqueous solution of $KClO_4$ + KCl at 300K: (a) $^{35}$Cl-SI 8K, 0.24 Hz/pt, NS = 1070 ($ClO_4$) and 2200 (Cl); (b) $^{36}$Cl--SI 32K, 0.03 Hz/pt, NS = 2800 ($ClO_4$) and 2300 (Cl); (c) $^{37}$Cl--SI 16K 0.06 Hz/pt, NS = 6400 ($ClO_4$) and 15488 (Cl).

The corresponding NMR parameters are listed in Tables 2 and 3.

**Table 1**. NMR characteristics of chlorine isotopes

| Isotope | Spin $I$ | Quadrupole moment $Q$, barn | Magnetogyric ratio $\gamma$, $10^7$ rad $s^{-1}$ $T^{-1}$ | Resonance frequencies, MHz, in magnetic fields | |
|---|---|---|---|---|---|
| | | | | 4.6975 T | 7.042 T |
| $^{35}$Cl | 3/2 | $8.2 \times 10^{-2}$ | 2.6242 | 19.6080 | 29.410 |
| $^{36}$Cl | 2 | $-1.7 \times 10^{-2}$ | 3.0809 | 23.0216 | 34.530 |
| $^{37}$Cl | 3/2 | $-6.5 \times 10^{-2}$ | 2.1844 | 16.3225 | 24.476 |

The relaxation of chlorine isotopes is dominated by the quadrupolar mechanism, which implies that for the isotopes incorporated in the same compound, the relaxation times and linewidths are determined by the spin factor multiplied by the squared effective quadrupole moment:

$$f(I,Q) = Q^2(2I+3)/I^{\,2}(2I-1) \; = \begin{cases} 89.63 \times 10^{-60}\ \mathrm{m}^4 \ \text{for} \ {}^{35}\mathrm{Cl} \\ 1.68 \times 10^{-60}\ \mathrm{m}^4 \ \text{for} \ {}^{36}\mathrm{Cl} \\ 56.35 \times 10^{-60}\ \mathrm{m}^4 \ \text{for} \ {}^{37}\mathrm{Cl} \end{cases} \qquad (1)$$

The linewidths and $T_1$ for $^{36}$Cl would be expected to differ from those for $^{35}$Cl by a factor of 53.4 and for $^{37}$Cl by a factor of 33.5. The $^{35}$Cl-to-$^{37}$Cl linewidth ratio should be 1.59.

The experimental linewidth ratios (Table 2) are the following: $^{35}\Delta\nu / ^{36}\Delta\nu = 2.20/0.07 = 31.42$, $^{37}\Delta\nu / ^{36}\Delta\nu = 1.34/0.07 = 19.4$, $^{35}\Delta\nu / ^{37}\Delta\nu = 2.20/1.34 = 1.64$. The ratios predicted by equation (3) are fulfilled only for the $^{35}$Cl and $^{37}$Cl isotopes due to insufficient field homogeneity and accuracy of measuring the width of a very narrow $^{36}$Cl NMR line and the incorrect $^{36}$Cl quadrupole moment reported. In this context, we measured the spin-lattice relaxation times $T_1$ (Table 2).

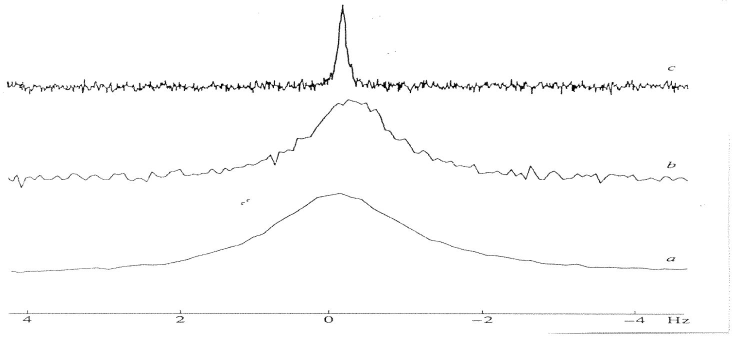

**Fig. 2.** NMR spectra (B = 4.6975 T) of an acetonitrile solution of $Bu_4NClO_4$ (3.3 M) at 300 K: (a) $^{35}$Cl--SI 4K, SW = 300 Hz, and NS = 8; (b) $^{37}$Cl--SI 16K, SW = 300 Hz, and NS = 16; (c) $^{36}$Cl—SI 16K, SW = 100 Hz, and NS = 8.

**Table 2.** $^{35,36,37}$Cl NMR chemical shifts, linewidths, and spin-lattice relaxation times of chlorine nuclides in an acetonitrile solution of $Bu_4NClO_4$

| Isotope | Chemical shift, ppm | Linewidth $\Delta\nu_{1/2}$, Hz | $T_1$, s | |
|---|---|---|---|---|
| | | | 4.6975 T (300K) | 7.042 T ((292 K) |
| $^{35}$Cl | 1007.30(4) | 2.20(5) | 0.157 | 0.180 |
| $^{36}$Cl | 1007.29(4) | 0.07(3) | 4.57 | 5.04 |
| $^{37}$Cl | 1007.25(4) | 1.34(5) | 0.249 | 0.297 |

Note: For $^{36}$Cl, signals were referenced to the $Cl^-$ signal of sample 1. Chemical shifts, linewidths, and $T_1$ were measured in a field of 4.6975 T at 300.0 K.

The $T_1$ values obtained are consistent with linewidth data following from equation $(\pi T_1)^{-1} = \Delta\nu_{1/2}$ for the quadrupolar mechanism: $^{35}\Delta\nu = (\pi{}^{35}T_1)^{-1} = (0.158\ \pi)^{-1} = 2.01$ Hz, $^{36}\Delta\nu = (\pi{}^{36}T_1)^{-1} = (4.57\ \pi)^{-1} = 0.07$ Hz, $^{37}\Delta\nu = (\pi\ {}^{37}T_1)^{-1} = (0.249\ \pi\ )^{-1} = 1.28$ Hz. Thus, we argue that the experimental linewidths are true. The ratio of relaxation times $^{37}T_1/^{35}T_1 = 1.59$ coincides with the ratio of squared quadrupole moments $(^{35}Q/^{37}Q)_2 = 1.61$. This result gives evidence for the quadrupolar mechanism of $^{35}$Cl and $^{37}$Cl relaxation in the $ClO_4^-$ anions; therefore, we may assume that the following relations are fulfilled for $^{36}$Cl: $2.29(^{36}Q/^{36}Q)^2 = {}^{36}T_1/{}^{35}T_1 = 4.57/0.157 = 29.10$ ; $2.29(^{37}Q/^{36}Q)^2 = {}^{36}T_1/{}^{37}T_1 = 4.57/0.249 = 18.35$. From this relationships, it follows that $^{35}Q = 3.56\,{}^{36}Q$ and $^{36}Q = 0.023$ barn and $^{37}Q = 2.83\,{}^{36}Q$ and $^{36}Q = 0.023$ barn at $|^{35}Q| = 0.082$ barn and $|^{37}Cl| = 0.065$ barn.

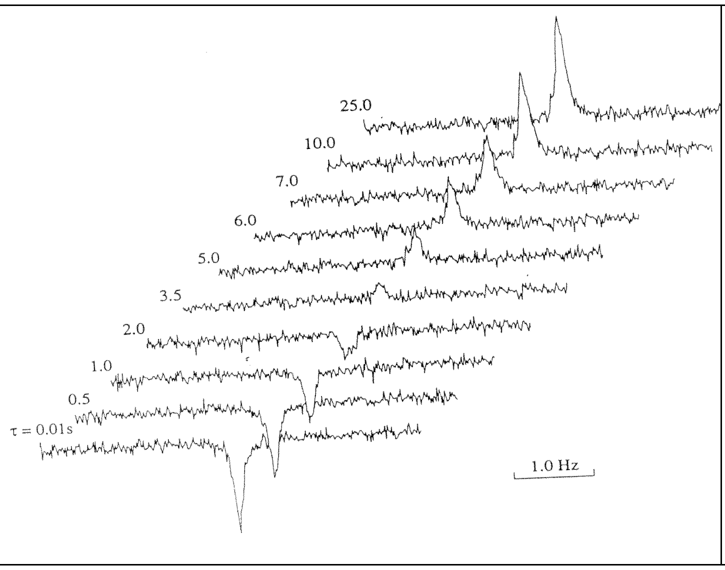

Fig. 3. Stacked plot of a FT inversion-recovery measurement of the spin-lattice relaxation time of $^{36}$Cl in a 3.3 M $Bu_4NClO_4$ solution in acetonitrile at 300 K. The delay times $\tau$ between the $\pi$ and $\pi/2$ pulses in the sequence $[(\pi\text{-}\tau\text{-}\pi/2)\text{-}5T_1]_n$ are given.

**Table 3.** $^{35,36,37}$Cl NMR parameters of Cl nuclides in an aqueous $KClO_4$ + KCl (0.1 M)

| Isotope | Chemical shift, ppm | Linewidth $\Delta\nu_{1/2}$ at 300K, Hz | |
|---|---|---|---|
| | | $ClO_4^-$ | $Cl^-$ |
| $^{35}$Cl | 1002.51(0.15) | 3.41(5) | 12.03(5) |
| $^{36}$Cl | 1002.81(0.1) | 0.12(3) | 0.41(5) |
| $^{37}$Cl | 1002.87(0.15) | 2.08(5) | 7.62(5) |

Note: Chemical shifts between the $ClO_4^-$ and $Cl^-$ signals for each of isotopes were measured in the field of 4.6975 T

The relaxation and $^{35,37}$Cl NMR linewidths in the $ClO_4^-$ and $Cl^-$ anions were comprehensively studied in both aqueous and nonaqueous solutions [5-8]. To compare the theoretical and experimental $T_1$ values, the corresponding values extrapolated to infinite dilution $T_1^0$ are usually used. For example, $^{35}T_1^0(ClO_4^-)$ is 0.27 s in aqueous solutions [6] and 1.19 s in acetonitrile solutions [5].

The EFG at $^{35}$Cl of the monatomic $Cl^-$ ion would be expected to be even smaller because of its spherical symmetry; hence, the relaxation times should be longer than for $ClO_4^-$. However, the relaxation time in aqueous solutions is $^{35}T_1(Cl^-) = 0.04$ s [6]. One of the possible reasons for this sevenfold difference in $^{35}T_1^0$ between $Cl^-$ and $ClO_4^-$ can be the magnitude of the Sternheimer antishielding factor $(1 + \gamma_\infty)$. The Sternheimer factor $(1 + \gamma_\infty)$ is known only for monatomic $Cl^-$ ions, but not for the $ClO_4^-$ ions. In terms of the Hertz electrostatic theory, the relaxation rate $T_1^{-1}$ of chlorine nuclides in the $Cl^-$ and $ClO_4^-$ anions is written as

$$T_1^{-1} = k8\pi^2/5(e^2Q/h)^2[\mu(1 + \gamma_\infty)P]^2C_s\tau/r^5, \qquad (2)$$

where $k$ is the scaling factor being 1 for spin 3/2 or 0.4375 for spin 2, $P$ is the polarization factor, $\mu$ is the dipole moment of the solvent molecule, $r$ is the distance between the chlorine nucleus and the dipole moment of the solvent molecule (as a point dipole) in the first coordination sphere. Then, according to equation (2), the ratio of relaxation rates or linewidths for any nuclide in $Cl^-$ and $ClO_4^-$ in the same solution is ${}^{(i)}T_1^{-1}(Cl^-)/{}^{(i)}T_1^{-1}(ClO_4^-) =$

$$= \{[1 + \gamma_\infty(Cl^-)]/[1 + \gamma_\infty(ClO_4^-)]\}*\tau(Cl^-)/\tau(ClO_4^-)*\, r^5(ClO_4^-)/\, r^5(Cl^-) \qquad (3)$$

where $i$ assumes the values 35, 36, or 37.

The ratio $r^5(ClO_4^-)/\ r^5(Cl^-) = (2.36+0.7)^5/(1.86+0.7)^5 = 2.44$, (in [12], this ratio was missing). According to the Debye-Stokes equation, the ratio of correlation times in solutions equals the ratio of cubic ionic radii $r_i$ ($Cl^-$) and $r_i$ ($ClO_4^-$):

$$\tau(Cl^-)/\tau(ClO_4^-)* = r_i^3(Cl^-)/\, r_i^3(ClO_4^-) = (1.86/2.36)^3 = 1/2.$$

Based on the experimental linewidths (Table 3), we may consider that:

$$^{35}\Delta\nu(Cl^-)/^{35}\Delta\nu(ClO_4^-) = 12.03/3.41*2=7.04/2.44 = 2.88, \qquad .$$

$$^{36}\Delta\nu(Cl^-)/^{36}\Delta\nu(ClO_4^-) = 0.40/0.11*2=7.28/2.44 = 2.98, \qquad (4)$$

$$^{37}\Delta\nu(Cl^-)/^{37}\Delta\nu(ClO_4^-) = 7.62/2.08*2=7.32/2.44 = 3 \qquad .$$

Since the Sternheimer factor for chlorine is much greater than one, it follows from equation (3) that

$$\gamma_\infty(Cl^-)/\gamma_\infty(ClO_4^-) = 3 \qquad (5).$$

Therefore, the Sternheimer factor for the perchlorate ion is smaller than that for the chloride ion by a factor of ca. 3. This result presumably reflects the different valence states of chlorine in $Cl^-$ (-1) and $ClO_4^-$ (+7).

With the parameters determined in this study, the low level detectable for $^{36}Cl$ is 0.5 ppm for concentrated samples, 15 ppm in 0.1 M chloride solutions; LLD for $^{36}Cl$ could be decreased by a factor of approx. 10 by addition of microamounts of paramagnetic ions ($Cu^{2+}$, $Ni^{2+}$).

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