NUCLEAR MAGNETIC RESONANCE SPECTRA OF THE HIGH-TEMPERATURE SOLID PHASE OF TETRA-n-HEXYL AMMONIUM PERCHLORATE*

EDWARD M. BARRALL II** AND T. T. HORIKAWA

IBM Research Laboratory, San José, Calif. 95193 (U.S.A.)

JOHN T. S. ANDREWS

Liquid Crystal Institute, Kent State University, Kent, Ohio 44242 (U.S.A.)

ABSTRACT

High resolution NMR (proton) spectra have been obtained of the solid phase of tetra-n-hexyl ammonium perchlorate between 364 and 379 K. Since it is well known that high resolution spectra cannot be obtained on true solids, the existence of four well-defined resonances (associated with the protons adjacent to the nitrogen, adjacent removed by one carbon, attached to three internal carbons and the terminal methyl protons) indicates that the hydrocarbon chains must exist in a state of free rotation. In the same temperature range (367.51 to 379.18 K) the ammonium and perchlorate positions are restricted to lattice points. A technique for the accurate measurement of temperature within the Varian HA100 NMR spectrometer is described. It is proposed as a result of the NMR study that the high temperature phase exists as a special case (ionic) of the plastic crystalline state. A search of the literature indicates that several other tetra-alkyl ammonium salts may exhibit the same phenomena.

INTRODUCTION

Tetra-n-hexyl ammonium perchlorate, in common with various other tetra-alkyl ammonium salts, has a low melting point as compared to other ionic materials, 379.18 K. In a recent work Andrews and Gordon[1] measured the heat capacity of the salt from 300 to 386 K. Three solid state transitions and fusion had been identified by microscopy and differential scanning calorimetry[2]. Examination of the heat capacity data presented by Andrews and Gordon indicates that the solids existing below and in the transition intervals up to the final solid phase transition at 367.51 K are relatively well behaved having good linear plots of heat capacity as a function of temperature. However, the heat capacity of the final solid phase (between 367.51 and 379.18 K (fusion)) is non-linear. This cannot be accounted for on the basis of

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purity as the sample was at least 99.94 mole % pure. Also, this final solid phase heat capacity is substantially depressed below the adjacent solid and liquid phases. For the purposes of later discussion the last portion of Andrews' heat capacity data are shown in Fig. 1.
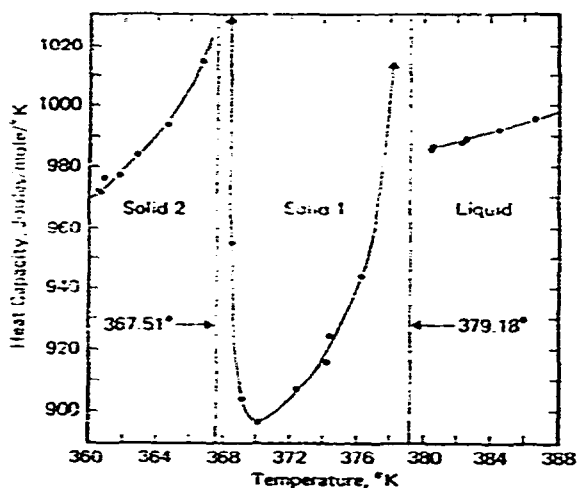

Fig. 1. Tetra-n-hexyl ammonium perchlorate heat capacities from Andrews and Gordon[1].

Such depressed heat capacities have been noted in the past for the smectic mesophase and some cholesteric materials[3,4]. This is not meant to imply that tetra-n-hexyl ammonium perchlorate is liquid crystalline at any point, but only that an unusual type of order may be present in the solid I (Andrews' nomenclature). In addition, the type of order in the system may be continuously changing as a function of temperature below the equilibrium melting point. This would account for the lack of linearity in the heat capacity slope as a function of temperature. It is possible to speculate that the n-hexyl chains may be free to rotate in phase I while the ionic nitrogen and perchlorate are residing on lattice points. Dilatometric data on tetra-n-amyl ammonium thiocyanate show an unusually high specific volume increment for the high temperature polymorph of the material[5]. This would tend to support, by analogy, the freely rotating chain hypothesis.

One of the present authors (E.M.B. II) has applied high resolution NMR to unusual solids. Rotational disorder in long side-chains was explored in detail for tristearin[6]. That material undergoes a series of phase transitions as follows: solid II → semiliquid → solid I → isotropic liquid. The semiliquid exists as an equilibrium state and was found to be due to the opening of the long stearic acid chains required to shift from the 90 to 60° base-plane form in solids I and II. During the several degrees in which the semiliquid exists as an equilibrium phase high resolution NMR spectra were obtained in which all of the protons expected in the C_{18} side-chain were giving sharp resonances. Not detected were the protons adjacent to the carbonyl and the protons on the glycerine backbone. The NMR spectra reverted to broad line when

the sample was heated into the equilibrium range of solid I. All of the expected protons were in clear evidence in the isotropic melt on further heating. The existence of the missing proton resonance in the melt gives good evidence as to the extent of chain disorder. The production of a high resolution resonance peak is adequate for assuming that a given functionality is as free to rotate as if in solution or melt. More precise measurement of resonance width would quantitate the degree of freedom.

The subject of this paper will be the consideration of n-hexyl mobility by NMR at elevated temperatures. In particular the transition from solid II to solid I to the melt will be considered.

EXPERIMENTAL

Instrumentation

All spectra were obtained on a Varian HA-100 NMR spectrometer equipped with a Varian V4341/V6057 variable temperature accessory and a Varian V6040 controller. The spectra were taken with the 100 MHz probe with sweep widths of 500 and 100 Hz (as shown on spectra) with a sweep time of 100 sec. The frequency response for the temperature measured curves was 5 Hz, R. F. attenuator set at 25 db, sweep offset of 441 Hz. The spectrum amplifier was set at 6000. The attenuation in the field multigauss sweep frequency was changed from 0.04 to 0.4 after the glycol hydroxyl protons were detected. The spectrometer was operated in the frequency sweep mode.

Sample preparation

The tetra-n-hexyl ammonium perchlorate (THEX) was a portion of the sample purified for the calorimetric study[1]. Briefly, it was made by reacting tetra-n-hexyl ammonium iodide with perchloric acid in aqueous ethanol solution. It was then purified by two precipitations in the presence of excess perchloric acid, one recrystallization from ethanol and water and twice from diethyl ether–acetone. After vacuum drying the sample was zone refined through 100 passes. The purity of the calorimetric sample was measured by fractional fusion and found to be 99.94% (mole).

Sample mounting

Solution NMR spectra of THEX were obtained in the usual 4 mm i.d. sample tubes. The material was dissolved in deuterated chloroform to give a 10% solution and tetramethylsilane was added as an internal lock. Obviously, for melt sample scans and runs at various temperatures the lock signal generating compound cannot be added directly to the THEX; it would be counted as a gross impurity and completely upset polymorphism. Therefore, for the NMR spectra of the melt, where exact temperature need not be known, hexamethyl disiloxane was placed in a 1 mm capillary located in the center of the molten THEX contained in a 4 mm NMR tube. The hexamethyl material was used as it has a higher boiling point than tetramethylsilane.

The Varian variable temperature accessory, V4341/V6057, and V6040 controller are extremely difficult to calibrate with any degree of accuracy with respect to absolute temperature. It is usually necessary to measure the effective temperature by inserting a tube of ethylene glycol, obtaining an NMR spectrum and measuring the frequency separations between the methylene and hydroxy protons. A graph of separation as a function of temperature is supplied by Varian (see also ref. 8). The ethylene glycol tube is removed and the sample inserted. Since the heat exchange medium between the heater, sample and controlling temperature detector is air, any small disturbance as to flow will seriously affect the temperature. The dial settings on the V6040 may be calibrated with ethylene glycol but cannot be relied upon to be reproducible to better than ±2°C. This condition is most unsatisfactory for the type of measurement contemplated in this study. To overcome this problem a concentric sample tube was fabricated as shown in Fig. 2. The sample was placed as a powder in the central 2 mm i.d. tube and ethylene glycol jacket in the outer 4 mm i.d. standard NMR tube.

18 cm

Plastic Centering Cap

Ethylene Glycol

Sample
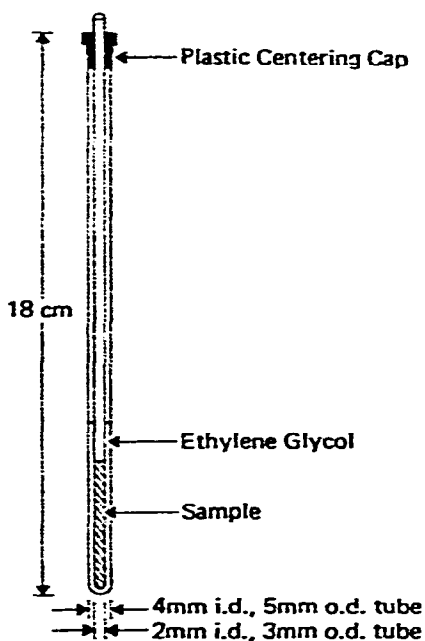
4mm i.d., 5mm o.d. tube
2mm i.d., 3mm o.d. tube

Fig. 2. Ethylene glycol jacketed tube for NMR temperature measurement.

Thus, the spectra of the THEX and ethylene glycol were obtained superimposed with the glycol acting as both the temperature detector (resonance separation of the above protons) and secondary heat exchange fluid to the THEX. The hydroxyl protons in the ethylene glycol were used as an internal lock for the Varian HA 100 NMR. Fortunately, little overlap occurred between glycol resonances and sample resonance. With this arrangement a dial setting on the V6040 was made, five minutes allowed for temperature equilibration and an NMR spectra rapidly taken. On that record were both the resonances to be measured and the resonances necessary for tem-

perature determination. The temperature was accurate to at least ±0.1 °C, with the accuracy limited by the precision with which the glycol proton resonance separation could be measured in Hertz. In addition, the hydroxyl proton resonance intensity acted as an internal standard for the comparison of spectra one with another. To avoid the effects of supercooling, all samples were *heated from* the well-defined phase 2, *never cooled* from the melt.

RESULTS

The solution form and melt form spectra of THEX are shown in Figs. 3 and 4. The resonance assignments are shown on the figures and the nomenclature, peaks I, II, III, IV, will be used for the remainder of the text. The resonance peaks in the melt are broadened probably due to dipolar coupling. However, peak II protons in the melt are much better resolved than in solution. A combination of coupling and temperature effects has caused the melt spectrum to shift upfield by an average of 46 cycles. Not all resonances are shifted by the same amount; peak I protons are shifted by 52 cycles. These numbers are corrected for the difference in lock frequency between TMS and HMDS of 6 cycles.

The individual peaks in the solution and melt samples were intergrated by planimeter and the relative proton concentrations were calculated and are shown expressed as percentages in Table 1. Although some internal variation is noted due to overlapping of peaks, deviations are restricted to ~5% at maximum. The critical ratios between peaks I and IV (2/3) and I and the sum of II and III (1/4) are preserved. The differences between solution and melt figures can be accounted for on the basis of different degrees of overlap.
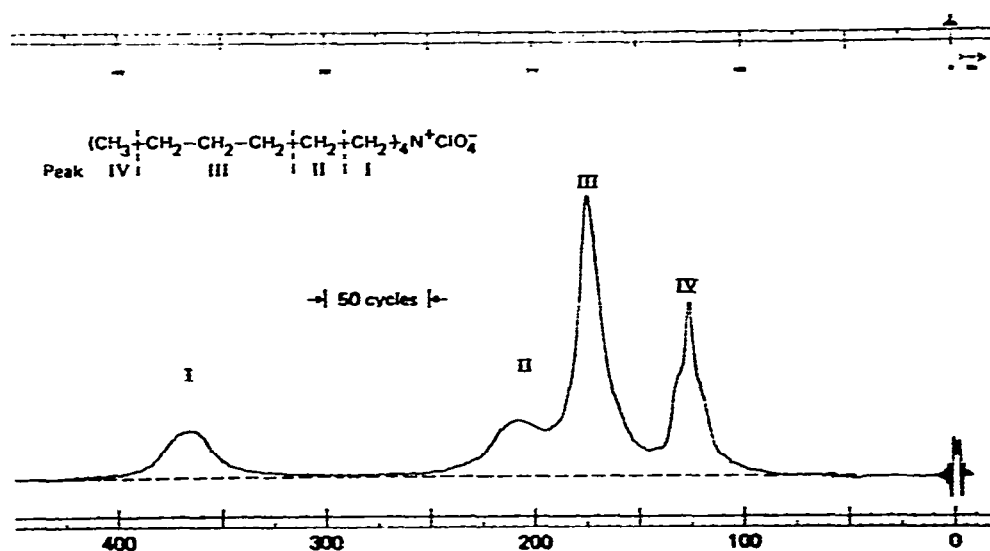

Fig. 3. Tetra-n-hexyl ammonium perchlorate NMR spectrum run as the melt (401.3 K).
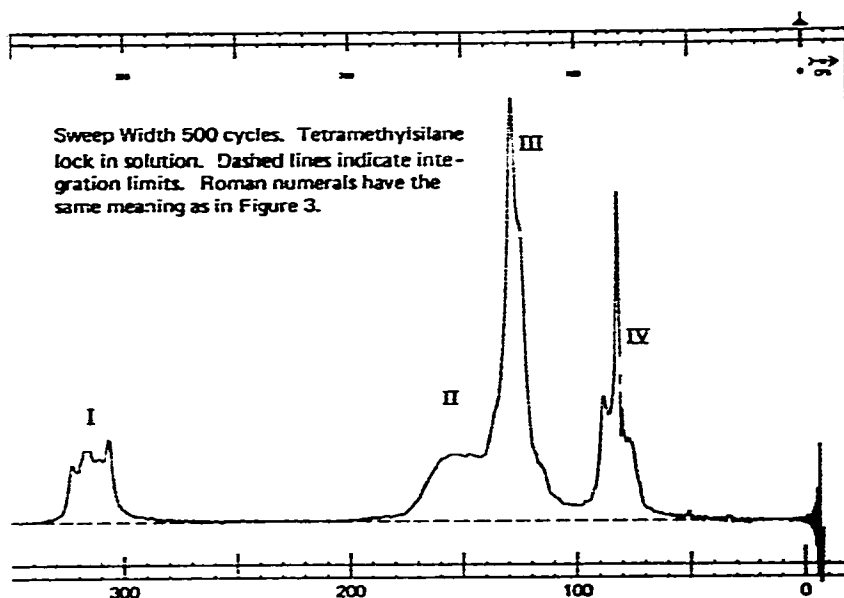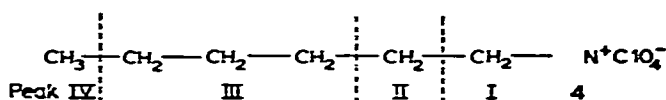
Fig. 4. Tetra-n-hexyl ammonium perchlorate NMR spectrum run in deuterated chloroform 10% solution.

TABLE 1

PROTON CONCENTRATION DATA FOR
TETRA-n-HEXYL AMMONIUM PERCHLORATE

$$CH_3 \mathbin{\vert} CH_2 \mathbin{—} CH_2 \mathbin{—} CH_2 \mathbin{\vert} CH_2 \mathbin{\vert} CH_2 \mathbin{—} N^+ClO_4^-$$

Peak IV   III   II   I   4

Peak no.	Proton concentration (%)		
	Calculated	Found	
		Solution[a]	Melt[b]
I	15.40	14.7	13.3
II	15.40	16.2	15.6
III	46.15	46.4	46.8
IV	23.05	22.6	23.8

[a] ~10% in $CDCl_3$. [b] Spectrum taken at 401.3 K.

Figures 5 and 6 show superimposed spectra obtained at different temperatures on a 1000 cycle sweep width. The ethylene hydroxyl proton lock appears downfield as the lock marker. Spinning side bands are apparent on both sides of the lock. The first major resonance is due to the glycol methylene protons. The separation in cycles between this peak and the lock determines the temperature. Directly upfield of
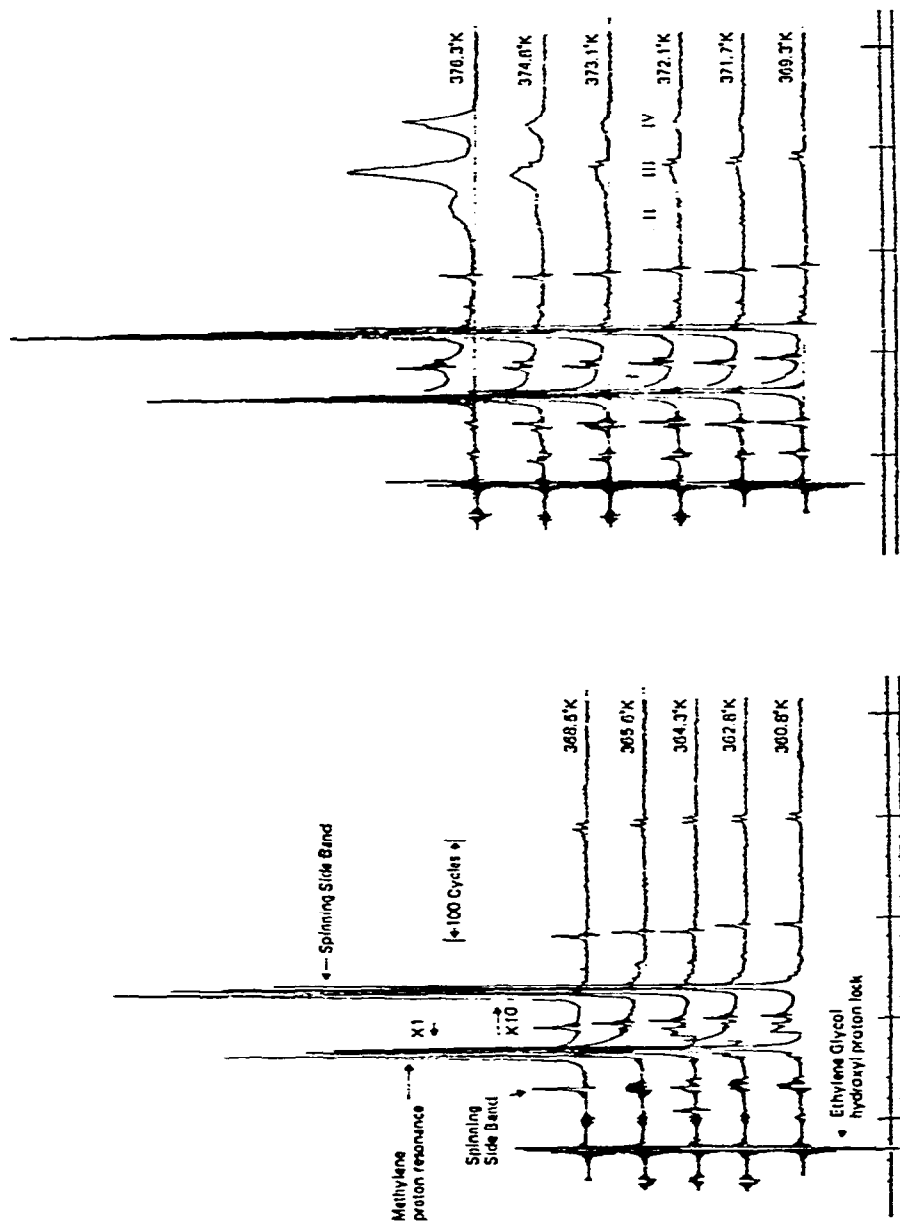
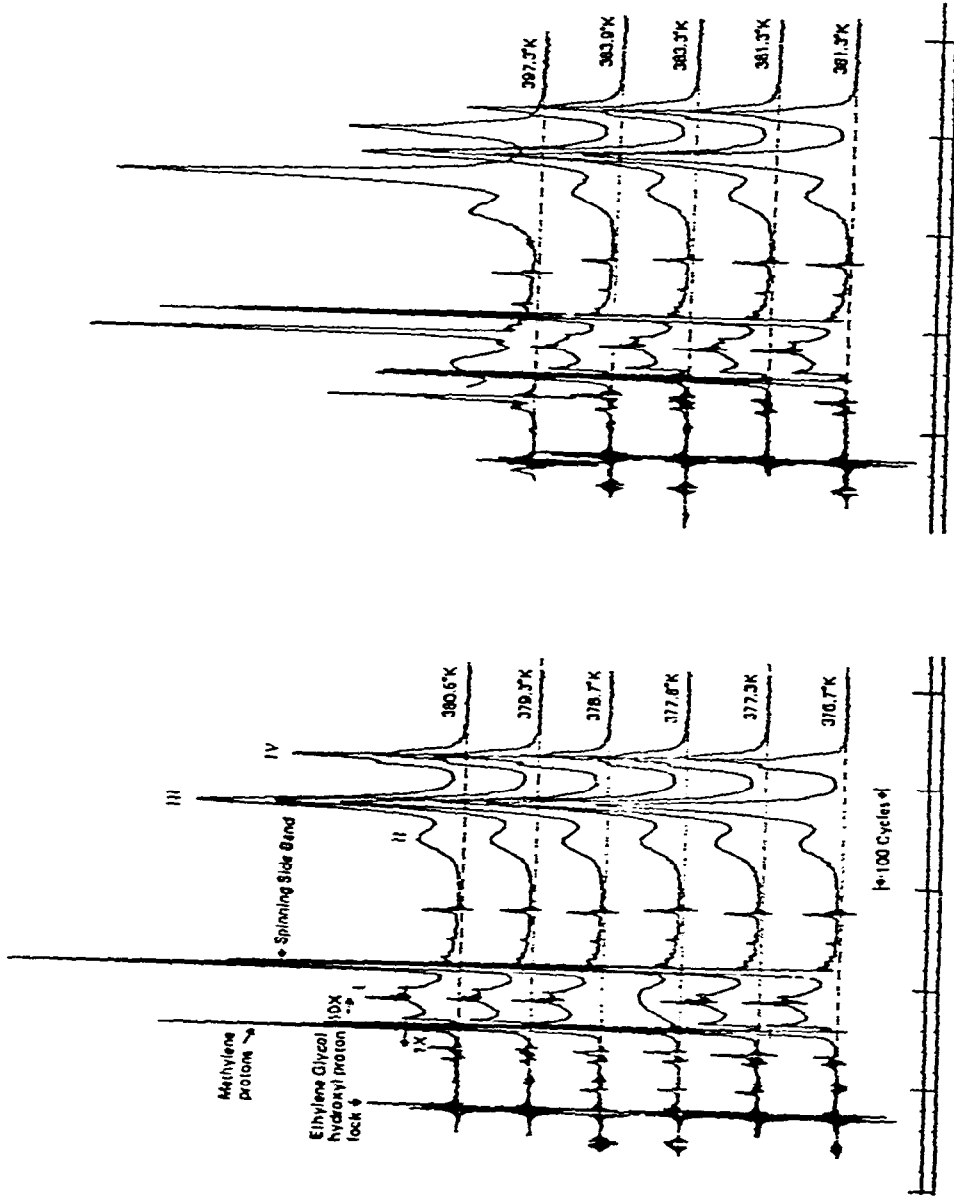Fig. 5. Tetra-n-hexyl ammonium perchlorate NMR spectra as a function of temperature.

Fig. 6. Tetra-n-hexyl ammonium perchlorate NMR spectra as a function of temperature.

the methylene proton resonance the amplification was increased ten-fold. The next major peak (actually minor on the previous scale) is a spinning side band, which partially overlaps the resonance peak I.

The presence of the glycol methylene protons as an internal standard permits intercomparison of the separate spectra on the basis of concentration of individual proton types. To accomplish this the individual peak heights were measured on each spectrum for peaks I to IV and the glycol methylene resonance. The heights of peaks I to IV were then divided by the appropriate glycol peak height and these are illustrated in Figs. 7–10. There is clear and direct evidence for the rapid appearance of resonance in the smooth and increasing series of characteristic curves in solid I. Unfortunately, complete observation of peak I is obscured by a non-THEX resonance below 376 K.
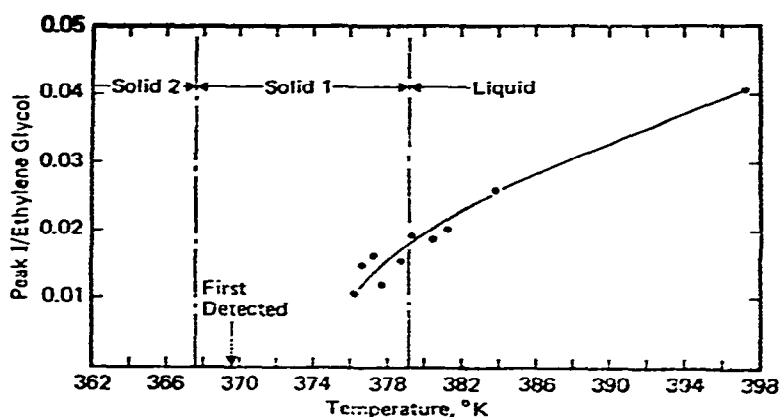

Fig. 7. Variation of peak I (protons adjacent to the nitrogen) intensity as a function of temperature.
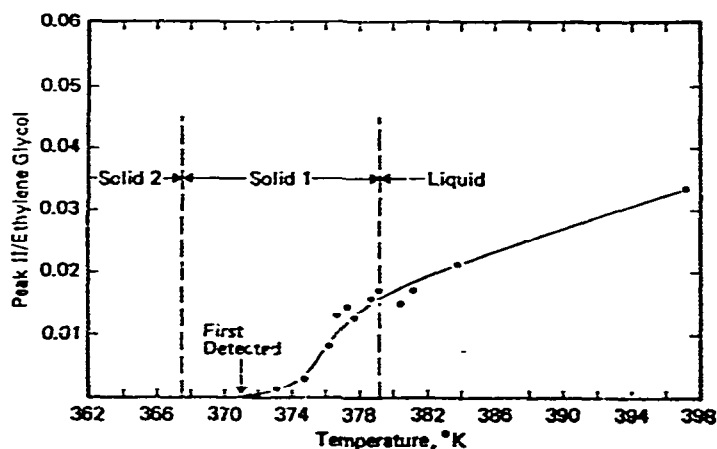

Fig. 8. Variation of peak II (protons removed by one carbon from the nitrogen) intensity as a function of temperature.
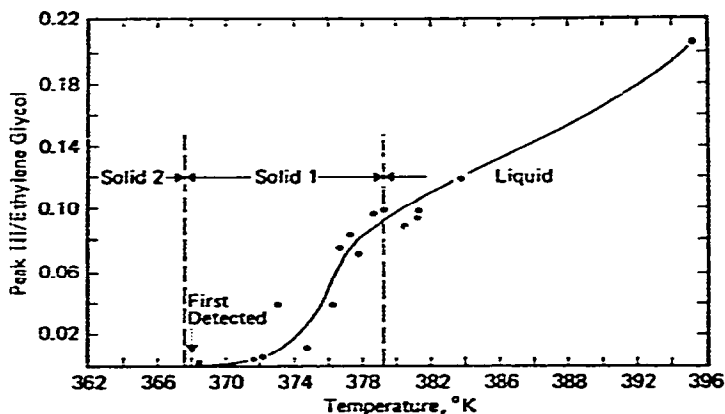
Fig. 9. Variation of peak III (internal proton) intensity as a function of temperature.
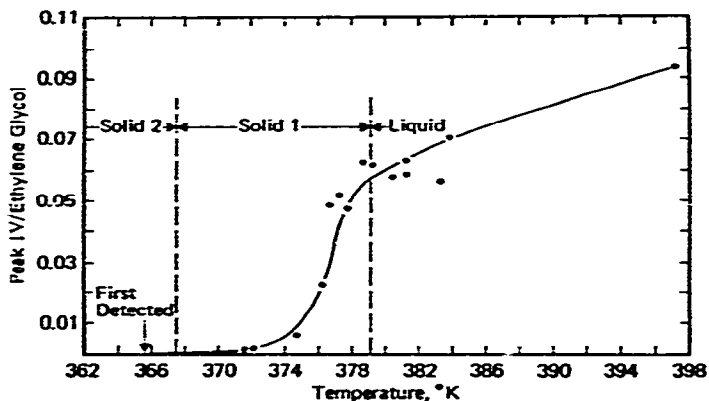

Fig. 10. Variation in terminal methyl proton intensity as a function of temperature.

Relative peak height fractions were obtained in the melt without side-band interference by conventional NMR tube work with a sample at ~ 372.3 K. In this case the individual peak heights for I to IV were measured and summed from the spectrum shown in Fig. 11. The individual heights were divided by the sum to obtain the data shown in Table 2. The high temperature melt spectrum (Fig. 3) was treated similarly. From Table 2 it is apparent that the ratios of individual proton types are sensibly constant from near first appearance well into the molten phase. By analogy to the tristearin studies[6] the resonance due to protons adjacent to the nitrogen could develop to a lesser extent in the solid I phase than in the melt, due to local hindrance and/or coupling. In tristearin the long chains "melted" back only to the protons adjacent to the carbonyl. These protons did not appear until the high temperature isotropic melt was reached. Table 2 shows that once a hexane chain becomes free to rotate in a liquid-like manner the whole chain has a characteristically short relaxation time with no carbons frozen in. However, terminal methyl protons are detectable in the absence of protons two degrees into the lower temperature phase 2 (see Fig. 10).
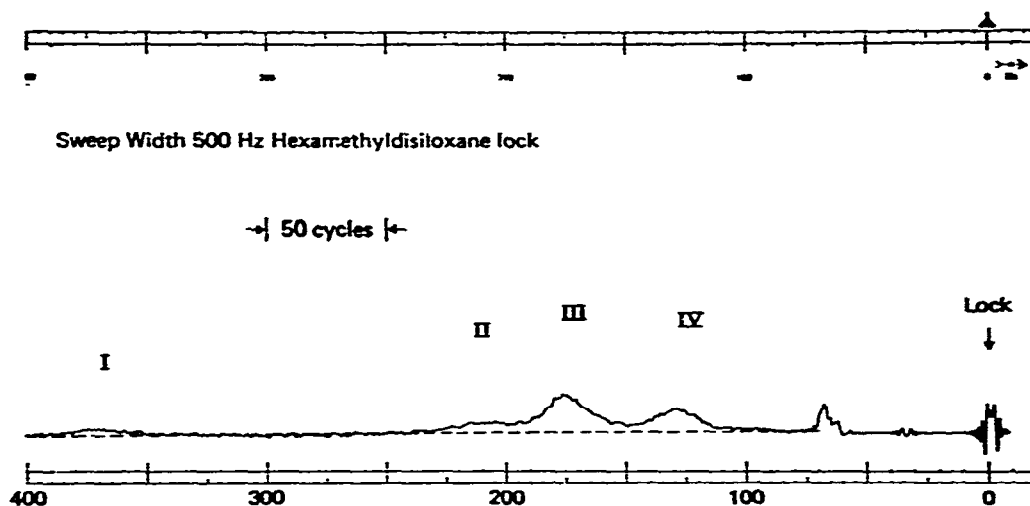
Fig. 11. Tetra-n-hexyl ammonium perchlorate NMR spectrum taken at 372.3 K showing resonances below the melting point without ethylene glycol interference.

TABLE 2

COMPARISON OF RELATIVE PEAK INTENSITIES
IN TETRA-n-HEXYL AMMONIUM PERCHLORATE AT TWO TEMPERATURES

Peak no.	Heigth fraction	
	372.3 K	401.3 K
I	0.084	0.080
II	0.127	0.090
III	0.486	0.500
IV	0.304	0.329

DISCUSSION

The high resolution proton resonances discussed in this paper show that the alkyl moieties are undergoing rapid movement at temperatures where the material is undoubtedly crystalline. These resonances "grow in" with increasing temperature throughout the range of solid 1 (shown in Figs. 7–10), and the increase in resonance intensity is correlated with the rise in heat capacity (shown in Fig. 1). Andrews and Gordon[1] have discussed possible interpretations of the transition entropy increments in THEX, and suggest that the alkyl moieties melt in a "kink-block" process which occurs in transition 3, while the ionic lattice persists until fusion. It seems likely that the motions of the alkyl chains are quite slow (on a 100 MHz time scale) when the chains first melt, so that the correlation time, τ_c, is too long for high resolution proton resonances to be seen. The rates of the molecular rotations will be subject to the Boltzman distribution leading to a corresponding distribution in τ_c values, which

will shift to lesser values as the temperature is raised. On increasing the temperature resonances should appear when τ_c reaches the "observable range", and the intensity of the resonances should increase as a greater proportion of the alkyl chains rotates more rapidly. The observed heat capacity rise is to be expected in a system of restricted rotors in which the rotation rates increase.

The final fusion of solid I is characteristic of the ammonium and perchlorate ionic lattice (cubic)[1]. An examination of the literature on fusion heats of the quaternary salts shows little variation in fusion entropy with the length of the alkyl chain[7], although large variations are noted in the solid phase transition entropies with the increment of a single carbon unit. Some small contribution to the translational mass entropy term is unavoidable as carbon-chain mass increases. However, the ammonium ion–anion separation is by far the larger.

The temperature at which peak III first becomes detectable is very close to the thermodynamic boundary of solids 2 and I, 0.5°C. This separation is trivial in consideration of the general low sensitivity of this type of proton NMR to considerations below about 3%. In all cases narrow line NMR resonances were detectable at temperatures below 370.2 K, the heat capacity inflex as measured by Andrews (see Fig. 1). The heat capacity range from 370.2 to 375 K is almost linear. This effectively rules out premelting due to impurities. The range would be very non-linear if impurities were present in THEX.

CONCLUSIONS

The proton resonance spectra reported here show that the alkyl chains attached to the ammonium ions of THEX are undergoing rapid "liquid-like" motion in the solid state prior to fusion, throughout solid phase I, and possibly into solid phase II. Specific resonances may be assigned to each set of equivalent protons in the moiety, and the constancy of the observed ratios of the intensities of these resonances suggests that a chain liquifies as a whole (although there is some evidence that the terminal methyl group may be undergoing more rapid rotation than the other portions of the chain). The change in resonance amplitudes is then due to the increase in rotational rates as the temperature is raised. THEX should be regarded as a material in which the disorder of the alkyl chains changes continuously with temperature between transition 3 and fusion (in contrast to the disorder of the tetrahedral perchlorate anions which changes discontinuously at transitions 1 and 2). The motion of the alkyl chains may be detected by NMR only at temperatures at which the rotation is sufficiently rapid to give a relaxation time short with respect to the time scale of the experiment.

The melting point at 379.18 K could then be regarded as the onset of translational freedom in a plastic crystal (melting of carbon tetrachloride or neopentane for example). The transition entropy is large compared to non-conventional spherical or symmetrical plastic crystal systems. However, the existence of ionic charge in the central atom (nitrogen) may account for this. Further work at elevated temperatures in a Raman spectrometer is in progress.

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