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NMR Studies of Na$^+$-Anion Association Effects in Polymer Electrolytes

by

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NMR Studies of Na^+-Anion Association Effects in Polymer Electrolytes

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ABSTRACT

^{23}Na nuclear magnetic resonance (NMR) measurements on poly(propylene oxide) (PPO) and siloxane based polymer electrolytes containing various sodium salts at a single nominal concentration are reported. In addition, differential scanning calorimetry (DSC) and electrical conductivity studies were carried out on the PPO materials. The NMR-determined mobile Na$^+$ concentrations and DSC results provide evidence for ionic aggregation effects which, for some samples, result in salt precipitation at elevated temperatures. ^{23}Na chemical shifts observed in solid state NMR due to mobile Na$^+$ ions are obtainable without the use of high resolution techniques, and exhibit strong dependences on anion and temperature. These results indicate that Na$^+$-anion interactions influence ionic transport as well as the number of available carriers.

INTRODUCTION

Solid complexes formed between polyethers and alkali metal salts, generally referred to as polymer electrolytes, have been investigated extensively in recent years [1-4]. Ionic conduction in amorphous polymer electrolytes is known to be intimately related to host segmental motions, although understanding of specific transport mechanisms is greatly complicated by the presence of significant cation-anion interactions in materials of moderately high salt concentration (4-20 ether oxygens/cation).

Spectroscopic evidence for ion-pairing or higher aggregation has been inferred from vibrational studies [5,6] while systematic conductivity vs. salt concentration measurements [7,8] have led to similar conclusions. ^{23}Na-nuclear magnetic resonance (NMR) has been shown to be an effective probe of Na^+ -ion mobility [9-11]. In most Na-salt containing polymer electrolytes, the NMR results have demonstrated the presence of both bound and mobile sodium. The bound ^{23}Na signal has previously been identified with large, relatively immobile clusters of ions, due to its similarity to the spectra of uncomplexed sodium salts [11]. Poly (propylene oxide) (PPO) has been chosen as one of the host polymers for this investigation because: i) it forms non-crystalline complexes with a variety of alkali metal salts; ii) some Na-salt-PPO complexes exhibit dramatic ionic aggregation effects which lead to salt precipitation (SP) at elevated temperatures[6,11-13]. The latter effect, while certainly not desirable for device applications, does provide a useful and direct means of monitoring the competition between cation solvation and ionic aggregation in the material.

EXPERIMENTAL

The sample preparation, differential scanning calorimetry (DSC), electrical conductivity, and ^{23}Na NMR instrumentation details are described elsewhere [9]. As in references 9,11, and 13, the host polymer was Parel-58 (Hercules, Inc.) which consists primarily (about 95 wt%) of high molecular weight PPO. Previous NaI-salt concentration studies of materials prepared with Parel-58 have shown in general that single phase samples exist only for compositions of approximately eight ether oxygens/Na [11]. Hence PPO_8NaX compounds, where $X = CF_3SO_3$, ClO_4, I, SCN, and a 1:1 mixture of I and CF_3SO_3, were prepared. For ^{23}Na chemical shift determinations, the spectra were internally referenced to a 1M aqueous NaCl solution.

RESULTS AND DISCUSSION

The DSC thermograms (recorded at 10K/min) for PPO-NaX containing various salts are displayed in Fig. 1a. All materials exhibit approximately equal values of central glass transition, T_g (about 273K), with a slightly lower temperature observed for the SCN sample. The presence of an additional glass transition in the vicinity of 213K, the value of T_g for "pure" PPO, indicates that the SCN complex exists as a single phase material only for O/Na smaller than 8. The high temperature endotherms observed in the I,

ClO_4, and SCN compounds are attributable to SP, while no corresponding feature is noted in the CF_3SO_3 sample. In an earlier publication[11], it was noted that the temperature at which SP occurs in the PPO complexes reflects the degree of interaction between cations and anions.

Figure 1b depicts the comparison between the CF_3SO_3, I and mixed CF_3SO_3/I compounds (The iodide shown is actually the composition $PPO_{16}NaI$, which has a slightly higher SP temperature than PPO_8NaI.). The mixed anion sample clearly exhibits an SP endotherm at about the same temperature as the iodide complexed material.

Interestingly, as shown in Figure 2a, the conductivity of the mixed anion complex shows a small, but discernable increase after SP. To emphasize this effect, the VTF equation[14]:

$$\sigma = AT^{-1/2}\exp\{-E_a/k(T-T_o)\} \quad (1)$$

was best-fit to the electrical conductivity data from 275-335K and is plotted as the solid line in figure 2a. The values of the fitting parameters were determined to be E_a=0.115, T_o=213K, and $\log_{10}A$=+0.64 and the RMS deviation in $\log_{10}\sigma$ was 0.005. The value of E_a is higher than the values found for PPO complexed with most Li salts and for $PPO_8NaCF_3SO_3$ as discussed below. However, the comparison is not particularly significant as the high temperature cutoff for the fit to the double doped material is arbitrary and the results are probably strongly affected by SP.

The rise of the electrical conductivity above the extrapolated VTF behavior at temperatures above the SP temperature is clearly seen. This is opposite the behavior observed previously for PPO containing a single ion [11,13]. However, these results can be understood if after SP of NaI the remaining ions have increased mobility. This is reasonable since after SP the oxygen/mobile sodium ratio is about 16 and thus the ions are moving through a polymer with a much lower glass transition temperature i.e. the temperature is further above T_g than before SP. This implies that $PPO_{16}NaCF_3SO_3$ does not phase separate into $PPO_8NaCF_3SO_3$ and uncomplexed PPO as is observed for PPO containing NaI [11]. However, this is not entirely clear at the present time as detailed concentration studies of the PPO: $NaCF_3SF_3$ system have not been performed.

In order to show that the behavior of the electrical conductivity is not intrinsic to PPO containing $NaCF_3SO_3$, its electrical conductivity was also studied and the results are shown in figure 2b along with the best-fit VTF curve. The data are well-behaved. In fact, E_a=0.092 was obtained for two samples and the value is relatively close to that reported for the electrical relaxation time for the alpha relaxation time for uncomplexed PPO and for the electrical conductivity for PPO containing various lithium salts [15]. Also, T_o=218K is once again found to be about 50K below the glass transition temperature and $\log_{10}(A)$=+0.49 is similar to results for other materials [15]. The RMS deviation in $\log_{10}\sigma$ was 0.01.

Reciprocal ^{23}Na free induction decay constants, $(T_2^*)^{-1}$

(proportional to the linewidth) for the mobile Na^+ ions in the PPO complexes are plotted as a function of temperature in Fig. 3. All samples exhibit similar behavior, the central features of which are motional narrowing above T_g to a linewidth minimum ocurring about 50K above T_g, and subsequent broadening as a result of extremely fast spin-lattice relaxation ($T_1 \sim 300$ µsec.). The temperature dependence of the ratio of mobile to bound sodium is plotted in Fig. 4. The ClO_4 and SCN complexes (Fig. 4a) show a gradual increase in mobile Na^+ concentration with increasing T and then a decrease as ionic aggregation begins to occur. The sharp decrease in mobile Na^+ concentration of the perchlorate observed at about 410K is clearly attributable to SP (the temperature at which SP occurs in the thiocyanate, 438K, is just outside the range of the NMR probe). Mobile/bound Na^+ data for the I, CF_3SO_3, and mixed anion samples are displayed in Fig. 4b. Ionic aggregation and, ultimately, SP effects are evident in the mixed anion compound, although a substantial mobile Na^+ concentration remains after SP. It is therefore likely that only NaI is present in the precipitate.

Mobile/bound ratios for NaX-poly(dimethysiloxane-ethylene oxide) complexes are plotted in Fig. 5. Previous ^{23}Na NMR studies of these materials [10] have shown motional narrowing behavior similar to that observed in PPO complexes although they do not exhibit SP effects. Nevertheless ionic aggregaton effects are apparent from the data in Fig. 5, which compares two samples that differ only in anion. Both materials have an ether oxygen/sodium ratio of 8. At all temperatures studied the CF_3SO_3 compound exhibits significantly greater mobile Na^+ concentrations than the CF_3COO sample. This result appears to be consistent with the relatively high dissociation energy of $NaCF_3COO$ as compared to the triflate salt. Similar measurements performed on amorphous poly(ethylene oxide) networks complexed with NaI and with $NaCF_3SO_3$ indicate that the triflate material exhibits consistently higher mobile Na^+ concentrations than the iodide [16].

^{23}Na NMR absorption spectra for PPO_8NaClO_4 at 413K are shown in Fig. 6. The doublet in the top spectrum, acquired with a 2s repeat delay, arises from Na^+ remaining in the complex and Na residing in the $NaClO_4$ precipitate. The bottom spectrum, acquired with a 10 ms delay, consists of only a single absorption associated with mobile Na^+ in the material, as the $NaClO_4$ signal is almost completely saturated. In addition to providing direct spectroscopic evidence of SP Fig. 6 also suggests that chemical shift effects may be resolvable without the use of magic angle spinning (MAS) techniques, particularly in the motionally narrowed region where the full width at half-maximum linewidth ranges from approximately 1 to 4 kHz.

Chemical shifts corresponding to the mobile Na^+ resonances (relative to aqueous NaCl) for several PPO complexes are plotted as a function of temperature in Fig. 7. The chemical shift clearly depends on the anion as well as temperature. With the exception of anomalous behavior of the perchlorate at the lower temperatures, all materials exhibit a downfield shift with increasing T. Similar results obtained in siloxane-based polymer electrolytes have been interpreted in terms of reduced cation-anion association at higher T [17]. According to the data in Fig. 7 the mixed anion compound appears to track the behavior of the triflate at lower temperatures and that of the iodide at higher T. One must exercise caution in drawing conclusions about the environment of the Na^+ ions in the mixed complex from this result, however it is clear from the previous DSC and NMR findings that the presence of triflate ions does not significantly inhibit SP of NaI.

The chemical shift thus far provides information about average ion association effects. The presence of specific configurations such as contact ion pairs or triplets in the above materials (with the exception of the large clusters which constitute the bound Na) cannot be established unambiguously by spectroscopic means at the NMR timescale. It has been suggested that a static contact Na^+X^- ion pair would yield a substantially quadrupole-broadened resonance [18]. Although previous observations of second-order quadrupole ^{23}Na lineshapes in polymer electrolytes have been made, the possiblity that they were attributable to interactions between Na and the siloxane backbone could not be ruled out [18]. In any case, the chemical shifts of the single and motionally narrowed resonances associated with the mobile Na^+ ions are clearly affected by time-averaged cation-anion interactions. However, attempts to determine even the average ionic environment of the cations are further complicated by solvent-induced chemical shifts associated with Na^+ - ether oxygen interactions, which have been shown to occur in *liquid polyether complexes* [19].

SUMMARY

The polymer electrolytes PPO_8NaX, where X = I, ClO_4, CF_3SO_3, SCN, and I/CF_3SO_3 (1:1), and siloxane-based polymers complexed with $NaCF_3COO$ and with $NaCF_3SO_3$ were investigated by ^{23}Na NMR with particular emphasis on probing cation-anion interactions. NMR measurement of mobile/bound Na^+ concentrations were found to yield useful information on ionic aggregation trends in the various materials. ^{23}Na chemical shifts of the mobile Na^+ resonance exhibited significant dependences on both anion and temperature, indicating that cation-anion association also plays an important role in the transport mechanism. DSC and electrical conductivity studies were carried out on the PPO materials. All of the results support the conclusions drawn from the NMR data.

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FIGURE CAPTIONS

Figure 1a) DSC thermograms (scan rate 10K/min) for PPO_8NaX where X = a) CF_3SO_3; b) SCN; c) ClO_4; d) I

Figure 1b) Comparison of DSC results for a) $PPO_8NaCF_3SO_3$; b) $PPO_{16}NaI$; c) $PPO_8Na(CF_3SO_3)_{0.5}(I)_{0.5}$

Figure 2a) Electrical conductivity of $PPO_8Na(CF_3SO_3)_{0.5}(I)_{0.5}$

Figure 2b) Electrical conductivity of $PPO_8NaCF_3SO_3$.

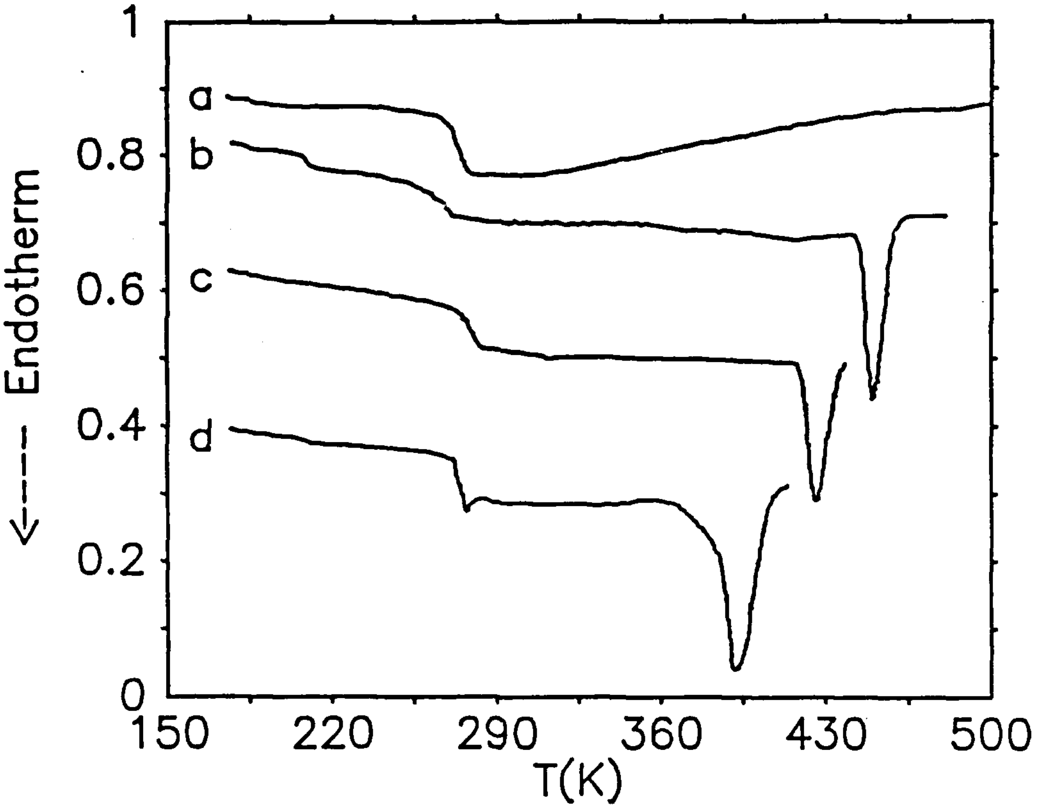
Figure 3) Reciprocal T_2^* (proportional to linewidth) temperature dependence of mobile Na^+ in PPO_8NaX where X = I(O); ClO_4 (+); SCN (*); CF_3SO_3 (◇); $(CF_3SO_3)_{0.5}(I)_{0.5}$ (⊕)

Figure 4) Mobile/bound Na^+ ratio vs. T in a) PPO_8NaClO_4 (+) and PPO_8NaSCN (*); and b) $PPO_8NaCF_3SO_3$ (◇); PPO_8NaI (O), and the mixed anion complex(⊕)

Figure 5) Mobile/bound Na^+ ratio vs. T in poly(dimethylsiloxane-ethylene oxide) complexed with $NaCF_3SO_3$ (*) and with $NaCF_3COO$ (□); ether oxygen/Na ratio is approximately 8.

Figure 6) ^{23}NMR absorption spectra in PPO_8NaClO_4 at 413K.
Top: Spectrum acquired with repeat delay of 2s, left half of doublet is attributable to $NaClO_4$ precipitate.
Bottom: Spectrum acquired with repeat delay of 10ms, salt signal is almost completely saturated.

Figure 7) Temperature dependences of ^{23}Na chemical shifts, relative to 1M aqueous NaCl, on PPO_8NaX where X = I (O); ClO_4 (+); CF_3SO_3 (◇); $CF_3SO_3)_{0.5}(I)_{0.5}$ (⊕)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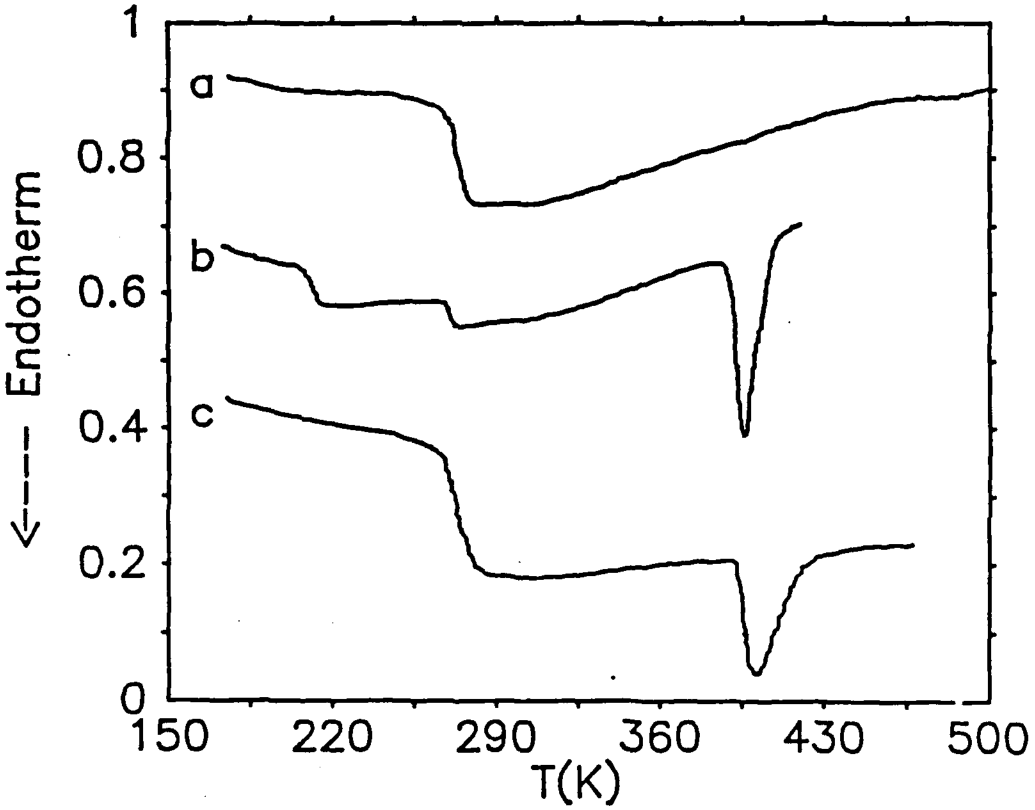


Fig. 1b

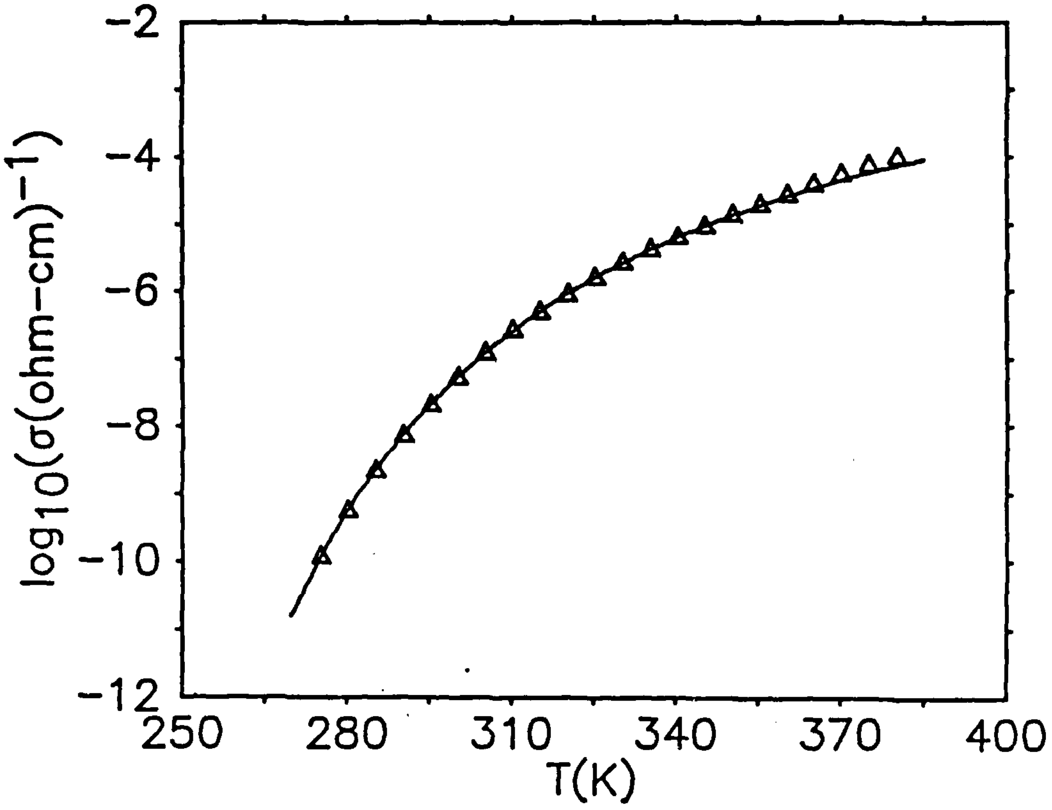
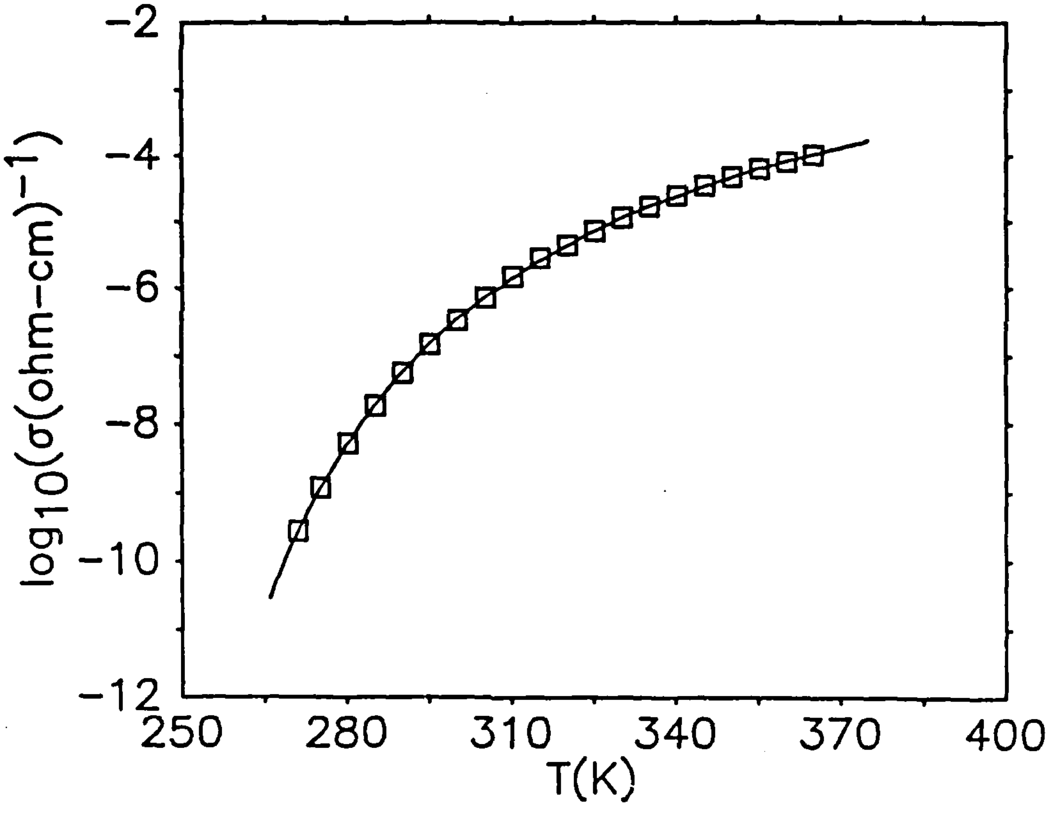


Figure 9



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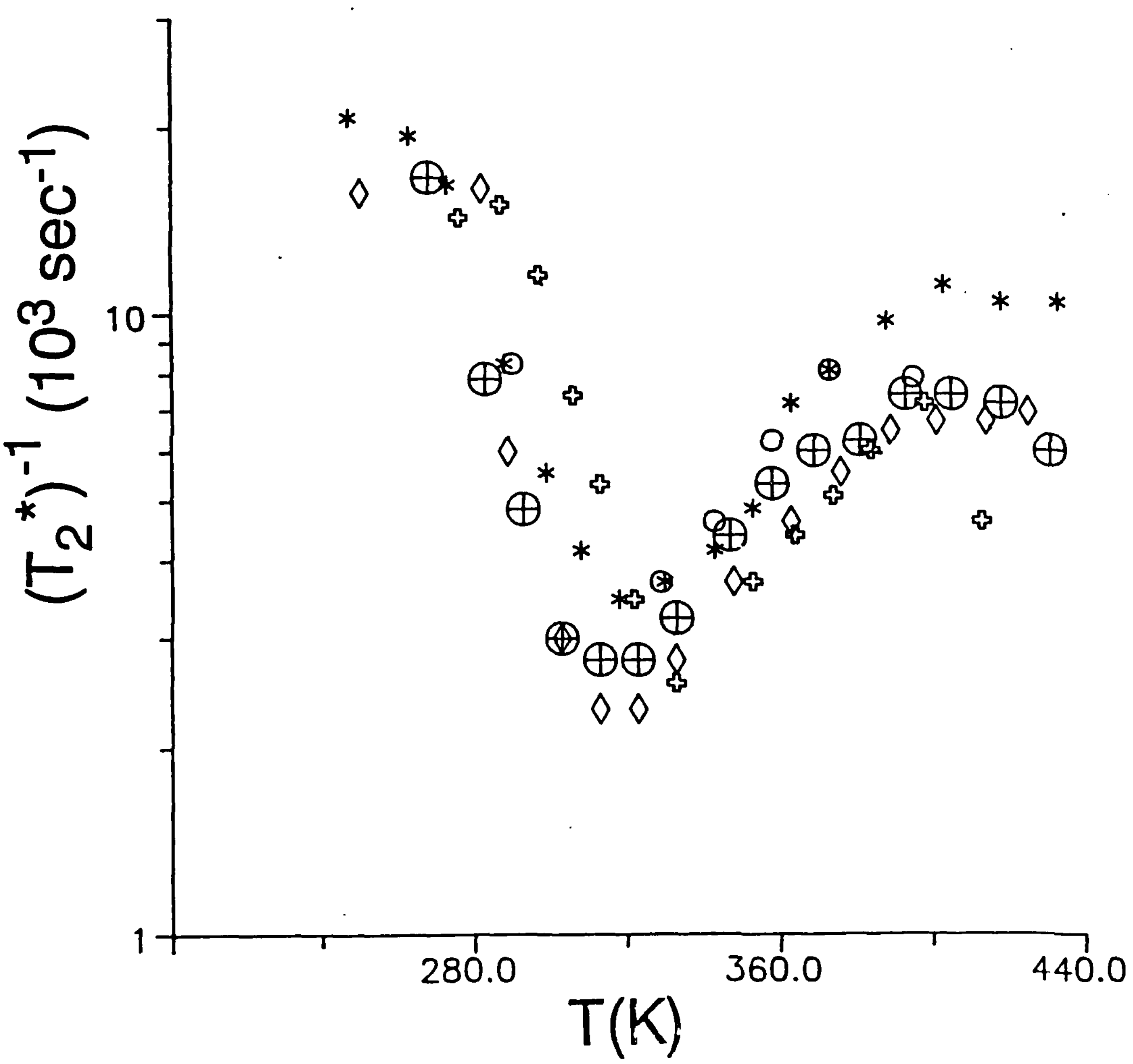

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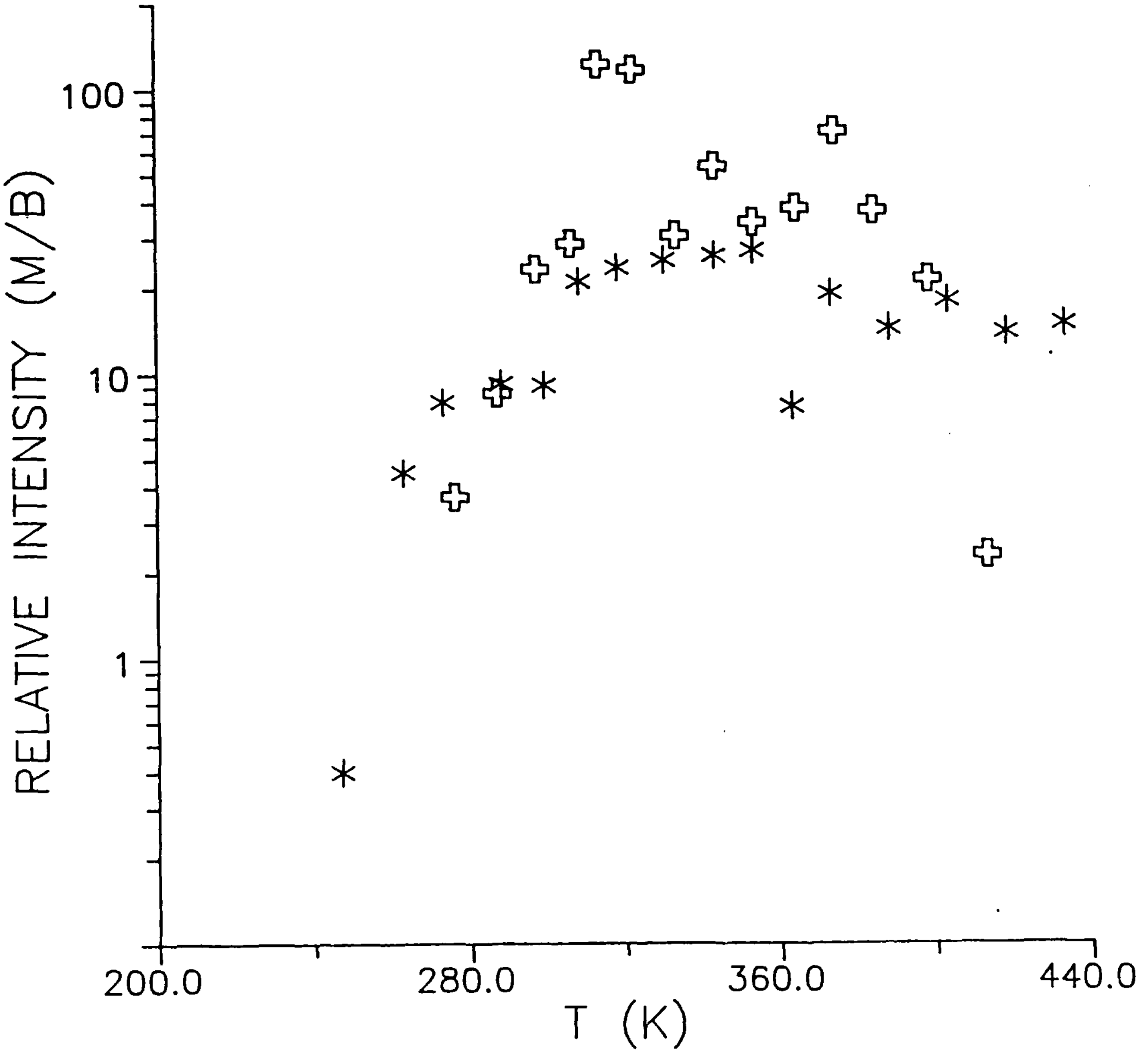
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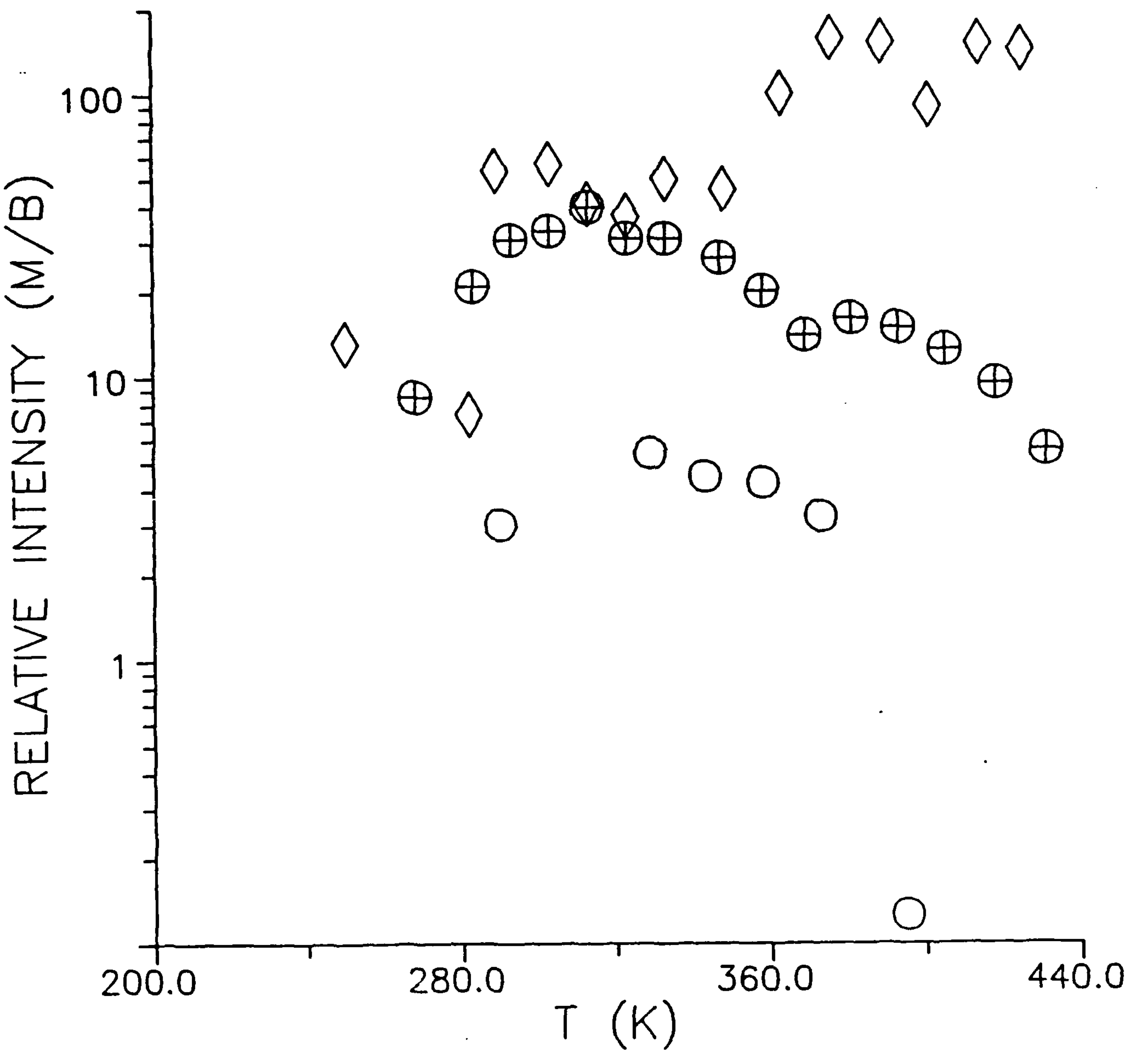
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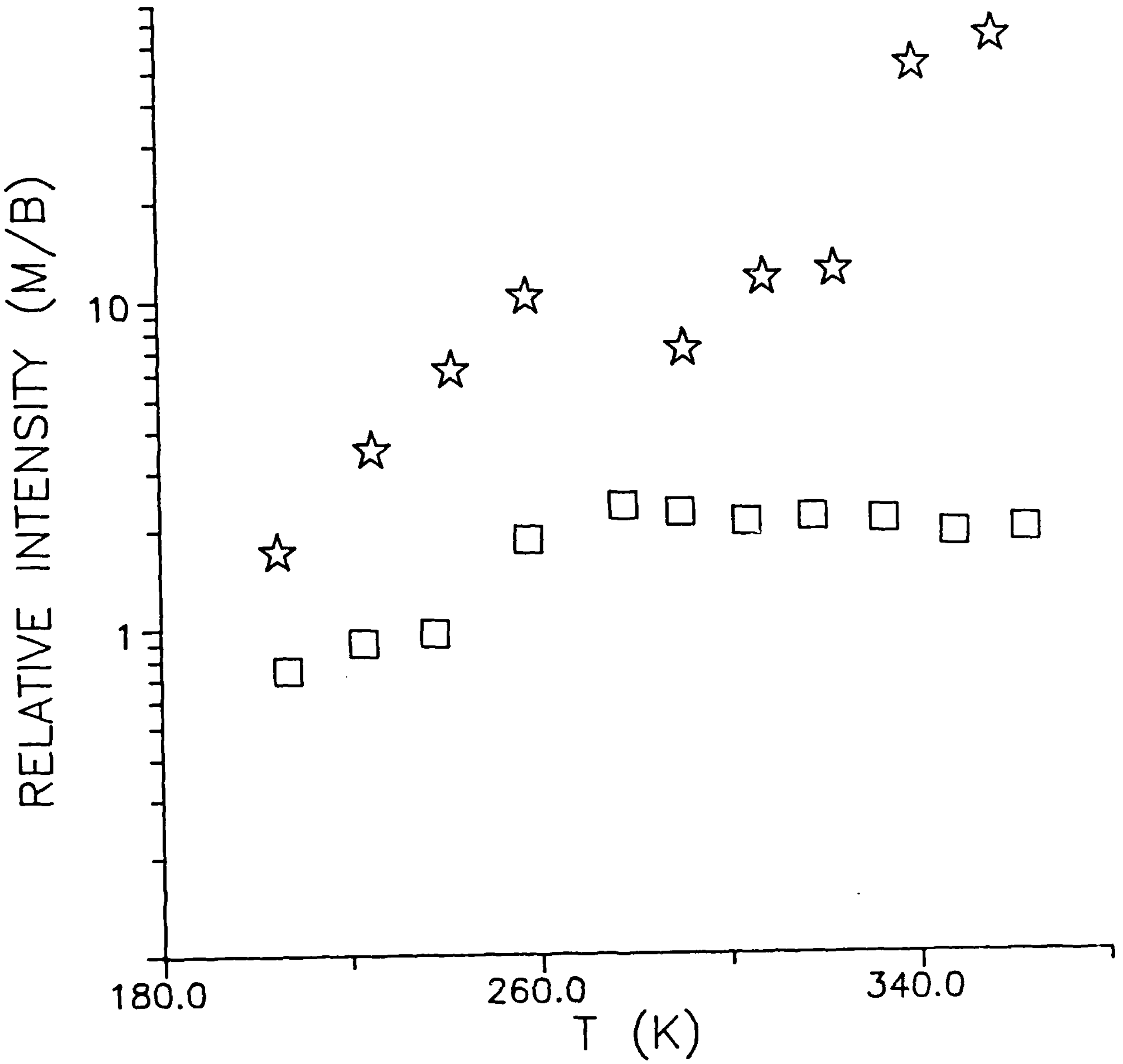
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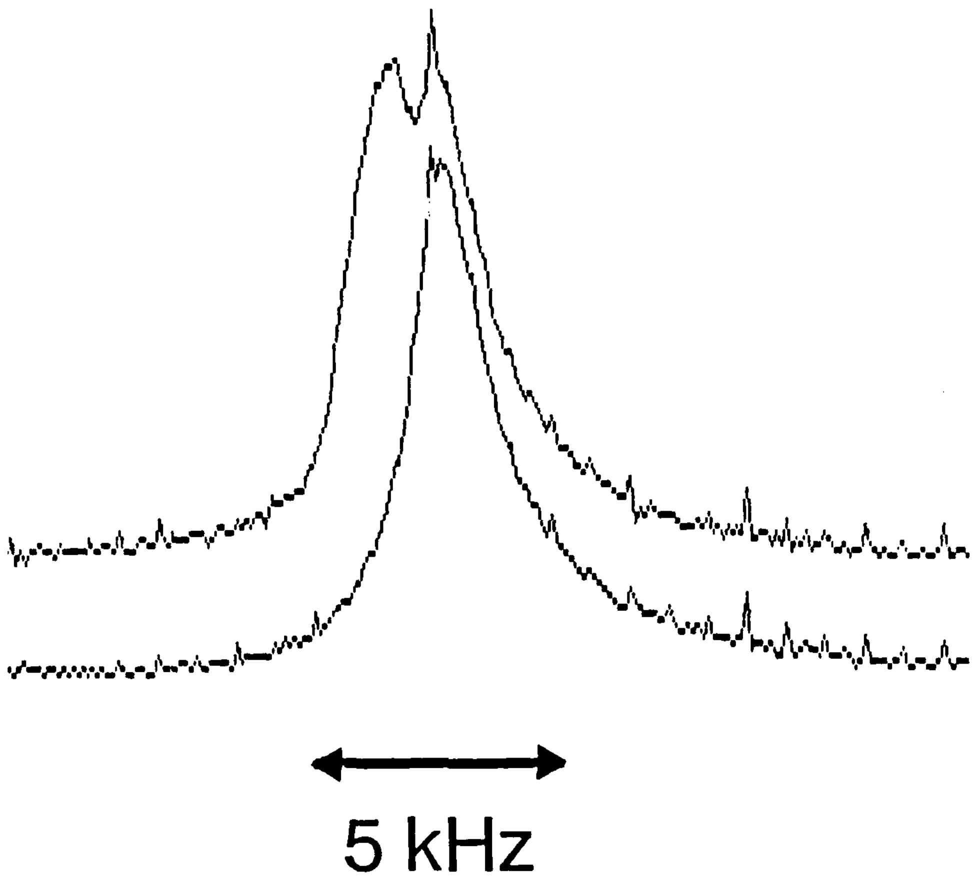
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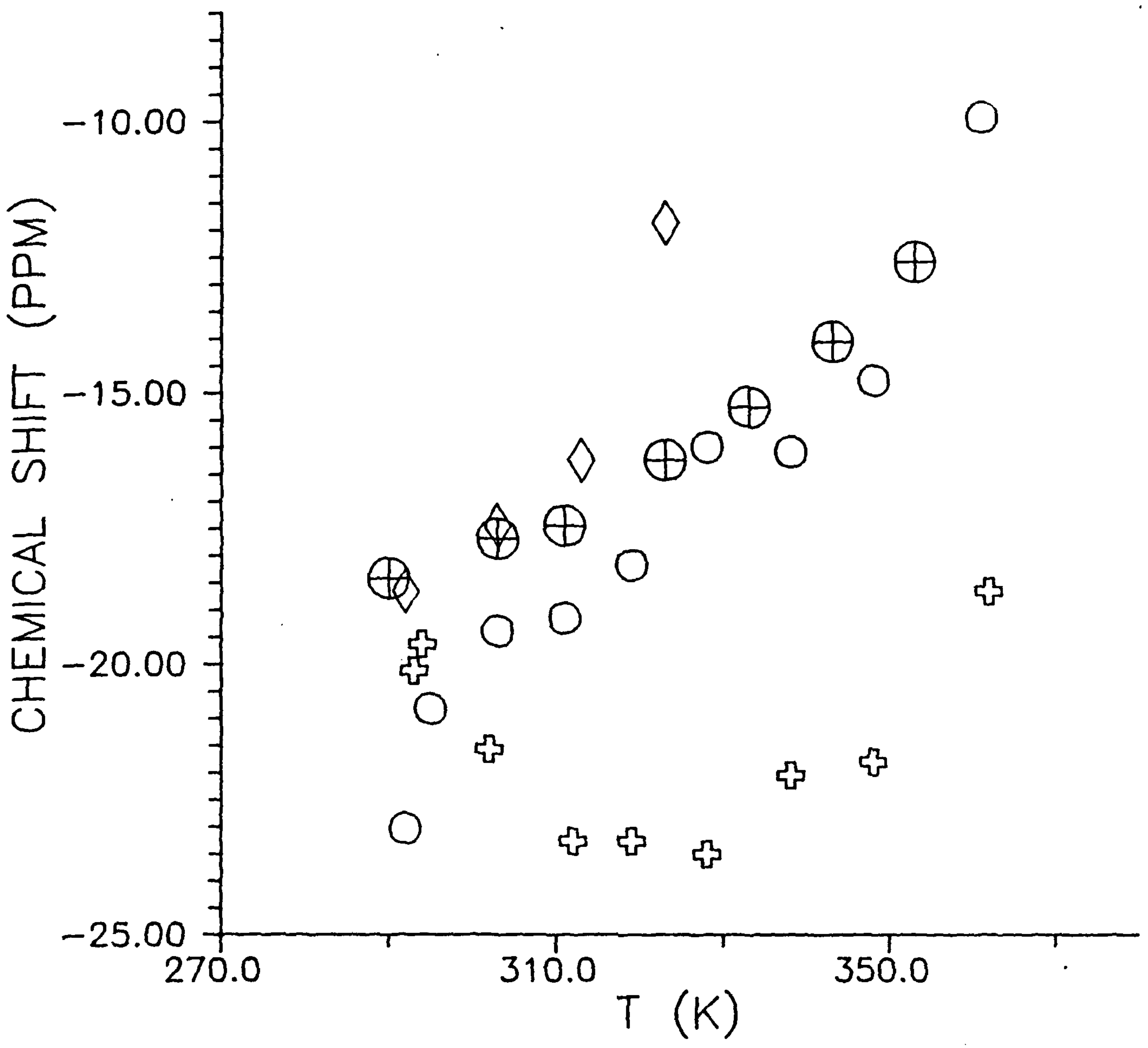
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