NMR Behaviour of Molten ^{115}Indium Chlorides

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Z. Naturforsch. **39a,** 1112 – 1114 (1984); received July 30, 1984

An NMR study was made of the ^{115}In nucleus in InCl, $InCl_2$, $InCl_3$ and in a mixture $InCl_3$ + NaCl. Chemical shifts and line-widths as a function of temperature were recorded in the molten state for all samples except $InCl_3$. As regards $InCl_2$, NMR results gave little support to the generally held view that $InCl_2$ is $In^{I}(In^{III}Cl_4)$ rather than $(In^{II}Cl_2)_2$.

High temperature NMR work has proved very important in providing information on the salt structure and on the nature of the bond. In particular, Tl salts [1 – 3] and Tl borate glasses [4] have already been studied.

The present work reports on measurements of the chemical shift and of its temperature dependence for the indium chlorides.

Experimental

A Varian (Model V 4200B) Wide-Line spectrometer was used in these experiments. The twelve-inch electromagnet (Model V 4012A) was operated by means of a Regulated Power Supply (Model V 2100) and a Fieldial Magnetic Field Regulator (Model V 2100 FR). The probe was of the single coil type with a twin RF bridge [5]. The furnace used a platinum wire resistance and was surrounded by a water-cooled jacket. Detailed information on the whole probe has already been given [6].

In the preparation of the salts 99.999% metallic In was employed as the starting material.

$InCl_3$: $2\,In + 3\,Cl_2 \rightarrow 2\,InCl_3$. At one end of a long tube, metallic In was heated at 200 °C under a stream of chlorine and nitrogen. The metal became first red (InCl), then yellow ($InCl_2$), and finally rapidly white ($InCl_3$). The temperature was increased to 450 °C, chlorine shut off and the compound purified by sublimation to the other end of the tube under the stream of nitrogen.

$InCl_2$: $In + 2\,HCl \rightarrow InCl_2 + H_2$. The compound was prepared by passing HCl through molten indium metal. The technique employed is similar to that used by Kenney [7] and described by Janz [8]. The analysis of the product gave In = 61.8% (calc. = 61.82), Cl = 38.2% (calc. = 38.18).

Concerning the melting point of $InCl_2$, some considerations are to be done. The values reported in the literature are largely discrepant. Klemm [9] studied $InCl_2$ samples prepared with different procedures and found different melting points spread over a wide temperature range from 235 °C up. Aiken [10] reported a sharp melting at 235 °C. Clarke [11] found that $InCl_2$ melts at 268 °C. Very close to this last value is that found by Chadwick [12] in the study of the In-Cl system. The cooling curve (obtained both by visual observation and DTA) shows that for this compound crystallization is a complex process, starting at 268 °C and ending at 235 °C. In this temperature range the liquid becomes immobile as if it were in a glassy phase. This hypothesis is supported also by the analysis of the line-width variation of the resonance signal with temperature.

InCl: $2\,In + InCl_3 \rightarrow 3\,InCl$. This compound was prepared by fusion of $InCl_3$ and metallic indium in stoichiometric ratio.

All three chlorides are deliquescent, and transfer operations were performed under a nitrogen atmosphere.

The reference for all NMR chemical shift measurements was a solution of $HInCl_4$ in ether approximately 1.5 M and prepared by ether extraction of a 4 M HCl aqueous solution of $InCl_3$. It has been shown [13] that this extract contains In as $InCl_4^-$. The symmetrical environment of this complex [14] gives rise to a resonance signal much sharper than from any other solution analyzed, so that it could be observed with an oscilloscope: in all other cases the use of a recorder with a lock-in amplifier was required.

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The effects of the DC current in the furnace were proved to be negligible: a polarity switch was inserted in the furnace circuit and no significant variation was observed in the signal recorded before and after reversing the polarity.

Results and Discussion

The ^{115}In resonance signal was looked for in the three chlorides InCl, $InCl_2$, $InCl_3$, and also in the 1:1 mixture $NaCl + InCl_3$. Only in molten InCl, $InCl_2$, and in the mixture a signal was detectable, whereas no resonance signal was found in any of the crystalline salts nor in molten $InCl_3$. This is probably due to line-broadening caused by the large quadrupole interactions of the indium nucleus with the electric field gradient in the anisotropic solids, which persists in molten $InCl_3$ [15]. By contrast, resonance was observed in molten $InCl_3$ to which excess of Cl^- was added (in the form of NaCl) thus causing indium to be mainly present as $InCl_4^-$.

The experimental results are summarized in Figs. 1 and 2 where the values of $\delta = (H_r - H_s)/H_r$ are referred to the ether extract at 25 °C. Moreover, Table 1 reports the temperature dependence of the chemical shifts along with their interpolated values at 400 °C, and the signal line-widths at the same temperature.

As it can be noted, all chemical shifts are upfield with respect to the reference: InCl has the largest shift ($-9.64 \cdot 10^{-4}$), a consequence of the shielding of the In(I) nucleus by two electrons as compared with In(III).

As regards the temperature dependence, indium chemical shifts in all three oxidation states show a linear downfield trend with temperature, the values of $d\delta/dT$ being in the range $(0.2-0.6) \cdot 10^{-6}\,K^{-1}$, very close to that observed for thallium salts (1).

Finally, the signal line-widths of molten $InCl_2$ suggest a few remarks. As it is apparent from Fig. 2, the line-widths of this salt are comparable (i.e. 4 G) with those for $InCl_4^-$ and InCl, but in the temperature range 268-235 line-width increases up to 6.25 G, and beyond 235 °C no signal is observable. This agrees with the observed thermal behaviour of $InCl_2$ on melting. Previous literature reports contradictory hypotheses on the structure of this salt. If the existence of a divalent indium ion is assumed, a paramagnetism due to the unpaired electron should be accepted: since indium dichloride has

Table 1. Interpolated values of the chemical shifts and line-widths at 400 °C along with the temperature dependence of δ. The ether-extract values are at 25 °C.

	$-\delta\ 10^4$	Line-width (gauss)	$d\delta/dT\ 10^6\ K^{-1}$
$InCl_4^-$ (ether)	0	2.37	–
$InCl_4^-$ (mixt.)	0.80	4.00	0.20
$InCl_2$	6.65	3.95	0.50
InCl	9.64	3.60	0.19

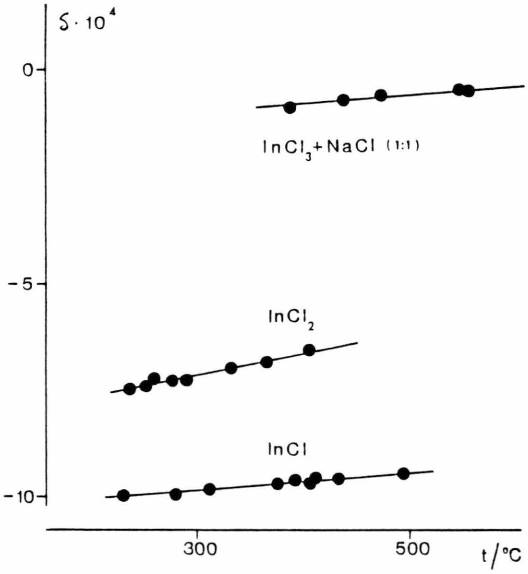


Fig. 1. Chemical shifts of ^{115}In as a function of temperature.

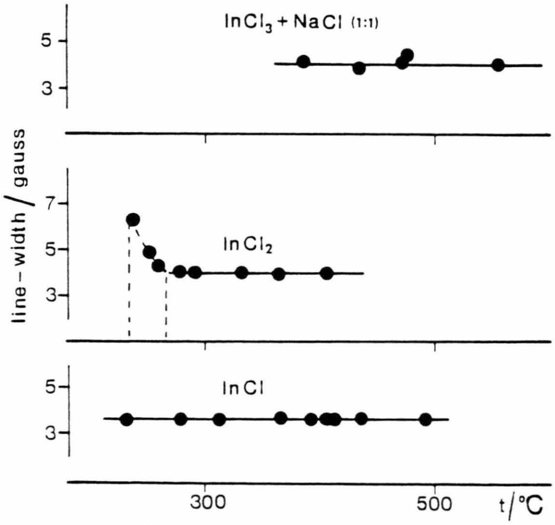
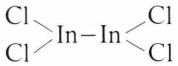


Fig. 2. Signal line-widths as a function of temperature.

been proved to be diamagnetic, an In–In bond must also be assumed [16]. Indium dichloride could also be a mixed valence double salt and still be diamagnetic. Thus for $InCl_2$ the following two possible structures were proposed:

A) $In^{I}(In^{III}Cl_4)$ B)



Structure B) was suggested by Klemm (16) and by others [17, 18], but generally [7, 10, 11, 12, 19] structure A) seems to be preferred. It should be noted that the analogous thallium salt shows a type A) structure.

In the present study a single resonance line, shifted toward the InCl, was always found for $InCl_2$ with a line-width comparable with the others. This result could be due to a very rapid resonance charge exchange between the two oxydation states, even though the position of the peak in this pale yellow melt makes it unlikely: the analogous thallium salt clearly shows two different peaks at NMR Tl analysis. Thus there is little support from the present study to the generally held view that $InCl_2$ is $In(InCl_4)$ rather than $(InCl_2)_2$.

Acknowledgement

This work was carried out at the Chemistry Department of the University of Chicago (mainly supported by an AFOSR grant) under the guidance of Prof. N. H. Nachtrieb to whom I am deeply indebted.

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