
Richard W. Briggs¹ and James F. Hinton¹,²

Received June 24, 1977; revised August 12, 1977

Solvation of the Tl⁺ ion in 0.005 M solutions of water/pyridine, water/dimethyl sulfoxide, and pyridine/dimethyl sulfoxide was studied with ²⁰⁵Tl NMR spectroscopy as a function of solvent composition and anion (NO₃⁻ and ClO₇⁻). Dimethyl sulfoxide solvated the Tl⁺ ion more strongly than did pyridine, despite the latter's greater electron-donating ability. This was explained in terms of structural effects, which were found to be large for all three binary solvent systems. Ion pairing was evident in the DMSO/pyridine and water/pyridine solvent systems in which the pyridine mole fraction was greater than 0.8.

KEYWORDS: Solvation; thallium-205 NMR spectroscopy; water; pyridine; dimethyl sulfoxide.

1. INTRODUCTION

The ²⁰⁵Tl nucleus has been shown to be a sensitive probe for NMR studies of ion solvation. Its chemical shift is very sensitive to solvent, concentration, and anion, and its T₁ has been shown to vary markedly with solvent. A study of thallous ion solvation in aqueous amide and mixed amide systems indicated that, in those mixed solvent systems, structural effects of the solution were important in determining preferential solvation. We wish to report the results of applying the donicity-structure analysis to binary systems involving pyridine and dimethyl sulfoxide.

¹ Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701
² To whom correspondence should be addressed
2. EXPERIMENTAL

Pyridine and dimethyl sulfoxide, both Mallinckrodt analytical reagent grade, were double-distilled under reduced pressure and stored in a vacuum desiccator over P₂O₅. Final-distillation boiling ranges were \( \leq 0.5^\circ C \). Water was double distilled and deionized.

Thallium nitrate (Fisher, purified) was recrystallized twice from double-distilled, deionized water, then dried at 110°C for 6–8 h in a vacuum oven (pressure ca. 7 mm Hg) before storing over P₂O₅ in a vacuum desiccator. Thallium perchlorate was similarly recrystallized and stored.

Nonaqueous solutions were prepared in a glove box under dry nitrogen atmosphere to exclude moisture.

Thallium-205 NMR spectra were obtained in 5-mm tubes at 24.0 ± 1.0°C with a modified Bruker HFX-90 spectrometer operating at 21.14 kG (2.114 T) with a ²⁰⁵Tl observation frequency of 51.94 MHz. An ENI 3100L broad-band amplifier was used to increase RF power from the transmitter. The spectrometer was interfaced to a Nicolet NMR80 minicomputer and a Diablo disk drive allowing operation in the pulsed FT mode. Thallium-205 resonance frequencies, relative to \(^1H\) of TMS, were determined by a method similar to that suggested by McFarlane⁹ and Harris and Kimber.⁹ Chemical shifts are referenced to infinite-dilution aqueous \( \text{Tl}^+\text{NO}_3^- \) as zero, with high-frequency shifts positive. TMS contained in a concentric capillary inside the 5-mm OD NMR tube served as an external \(^1H\) lock. Corrections for bulk susceptibility, which are negligibly small, were not made.

3. RESULTS AND DISCUSSION

The Gutmann donor number, a measure of the coordinating ability of a basic solvent, is defined as the negative of the enthalpy of interaction of a base with SbCl₅ when the two are dissolved in equimolar amounts in the inert solvent 1,2-dichloroethane.¹⁰ The donor number has been shown to correlate fairly well with the solvent-dependent chemical shifts of \(^{23}\text{Na},^{7}\text{Li},^{133}\text{Cs},^{139}\text{Cs},^{139}\text{Cs},^{205}\text{Tl}^{,5,6}\) Table I lists Gutmann donor numbers, thallium shift

<table>
<thead>
<tr>
<th>Solvent</th>
<th>DN₅SbCl₅</th>
<th>DN₂⁰⁵Tl⁺</th>
<th>ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>18.0</td>
<td>21.1</td>
<td>80.4</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>29.8</td>
<td>28.4</td>
<td>45.0</td>
</tr>
<tr>
<td>Pyridine</td>
<td>33.1</td>
<td>37.0</td>
<td>12.4</td>
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