COMPONENTS:
(1) Thulium chloride; TmCl₃; [13537-18-3]
(2) Ethanol; C₂H₆O; [64-17-5]
(3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Sakharova, Yu.G.; Ezhova, T.A.

VARIABLES:
Temperature

PREPARED BY:
T. Mioduski and M. Salomon

EXPERIMENTAL VALUES:

<table>
<thead>
<tr>
<th>t/°C</th>
<th>g/100 g sample 1</th>
<th>g/100 g sample 2</th>
<th>g/100 g sample 3</th>
<th>g/100 g sample 4</th>
<th>mean solubilities</th>
<th>mol kg⁻¹ c</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>42.09</td>
<td>42.20</td>
<td>42.26</td>
<td>41.91</td>
<td>42.11</td>
<td>1.897</td>
</tr>
<tr>
<td>30</td>
<td>41.06</td>
<td>41.16</td>
<td>41.12</td>
<td>41.14</td>
<td>41.11</td>
<td>1.821</td>
</tr>
<tr>
<td>40</td>
<td>41.70</td>
<td>41.73</td>
<td>42.09</td>
<td>41.83</td>
<td>41.83</td>
<td>1.876</td>
</tr>
<tr>
<td>50</td>
<td>41.17</td>
<td>44.21</td>
<td>44.44</td>
<td>44.50</td>
<td>44.33</td>
<td>2.077</td>
</tr>
<tr>
<td>60</td>
<td>47.08</td>
<td>47.26</td>
<td>47.46</td>
<td>47.35</td>
<td>47.29</td>
<td>2.340</td>
</tr>
</tbody>
</table>

a It is not clearly stated whether the mixture is 96.8 mass % or 96.8 volume % ethanol.

b Solubilities reported as grams of hexahydrate in 100 g of solvent.

c Molalities calculated by the compilers.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Isothermal method used. Equilibrium was reached after 3-4 h. Identical results obtained by approaching equilibrium from above and below. Two of the data points in the table obtained after 3 hours of equilibration, and the remaining two data points obtained after 4 h of equilibration.

The metal content in each aliquot taken for analysis was determined by complexometric titration with Trilon B.

Analyses of the solids withdrawn at 20°C, 40°C and 60°C showed the solid phase to be the hexahydrate: i.e. ethanol was not found in any of the solid phases.

SOURCE AND PURITY OF MATERIALS:
TmCl₃·6H₂O prepd by dissolving c.p. grade oxide in dil (1:3) HCl followed by evapn and crystn. The crystals were dried in a desiccator over CaCl₂, P₂O₅ and NaOH. The crystals analyzed for the metal by titrnm with Trilon B, and for Cl by the Volhard method. The hexahydrate melted at 162.4 - 163.5°C. 96.8% ethanol prepd by prolonged boiling of c.p. grade 93.5% ethanol with anhydr CuSO₄ followed by distn. Ethanol concn detd refractometrically and pycnometrically.

ESTIMATED ERROR:
Soly: results apparently precise to within ± 0.9 % (compilers).
Temp: nothing specified.

REFERENCES:
The solubility of TmCl₃ in 1,2-dimethoxyethane at 25°C was reported as 6.3 mass %.

The corresponding molality calculated by the compiler is 0.244 mol kg⁻¹.

The nature of the solid phase was not specified.
<table>
<thead>
<tr>
<th>COMPONENTS:</th>
<th>ORIGINAL MEASUREMENTS:</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Thulium chloride; TmCl₃; [13537-18-3]</td>
<td>Dzhuraev, Kh. Sh.; Mirsaidov, U.;</td>
</tr>
<tr>
<td>(2) Diethyl ether; C₄H₁₀O; [60-29-7]</td>
<td>Kurbanbekov, A.; Rakhimova, A.</td>
</tr>
<tr>
<td></td>
<td><em>Dokl. Akad. Nauk Tadzh. SSR 1976, 19, 32-4</em></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>VARIABLES:</th>
<th>PREPARED BY:</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/K = 293</td>
<td>T. Mioduski</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>EXPERIMENTAL VALUES:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>The solubility of TmCl₃ in diethyl ether at 20°C was reported as</td>
<td></td>
</tr>
<tr>
<td>0.053 mass %</td>
<td></td>
</tr>
<tr>
<td>The corresponding molality calculated by the compiler is</td>
<td></td>
</tr>
<tr>
<td>1.94 x 10⁻³ mol kg⁻¹</td>
<td></td>
</tr>
</tbody>
</table>

**AUXILIARY INFORMATION**

**METHOD/APPARATUS/PROCEDURE:**

Isothermal method employed. Equilibrium was attained within 24 h, and it was verified by constancy in the Tm concentration. The saturated solution and the equilibrated solid phase were analyzed. Tm determined by complexometric titration using urotropine buffer and methyl-thymol blue indicator. Chloride determined by titration with AgNO₃. The solid phase corresponded to TmCl₃.Et₂O (the etherate was dried under vaccum at 40°C prior to analysis).

**SOURCE AND PURITY OF MATERIALS:**

Anhydrous TmCl₃ prepared by the ethanol solvate method (no details given).

Ethyl ether was dried with Na and distilled from LiAlH₄.

**ESTIMATED ERROR:**

Nothing specified.

**REFERENCES:**
<table>
<thead>
<tr>
<th>COMPONENTS:</th>
<th>ORIGINAL MEASUREMENTS:</th>
</tr>
</thead>
</table>
| (1) Thulium chloride; TmCl₃; [13537-18-3] | Kirmse, E.M.; Zwietasch, K.J.  
| (2) 1,2-Diethoxyethane; C₆H₁₄O₂; [629-14-1] | |
| VARIABLES: | PREPARED BY: |
| T/K = 298 | T. Mioduski |
| EXPERIMENTAL VALUES: | |
| The solubility of TmCl₃ in 1,2-diethoxyethane at 25°C was reported to be | |
| 0.88 mass % | |
| The corresponding molality calculated by the compiler is | |
| 0.0323 mol kg⁻¹ | |
| The composition of the solid phase was given in terms of the Eu:Cl:ether ratio as | |
| 1:2.97:2.00 | |

**AUXILIARY INFORMATION**

**METHOD/APPARATUS/PROCEDURE:**
Isothermal method used. The anhydrous mixtures were equilibrated at 25°C for several days with frequent shaking.

The solid phase was dried in a vacuum desiccator over P₂O₅.

Tm was determined by complexometric titration using Xylenol Orange indicator. Chloride was determined by the Volhard titration method.

**SOURCE AND PURITY OF MATERIALS:**
Sources and purities of materials not given. The anhydrous chloride was obtained by the method of Taylor and Carter (1).

The solvent was prepared by the Williamson synthesis: i.e. by reaction of C₂H₅I with the monoethylether of ethylene glycol.

**ESTIMATED ERROR:**
No estimates possible.

**REFERENCES:**
1. Taylor, M.D.; Carter, C.P.  
COMPONENTS:
(1) Thulium chloride; TmCl₃; [13537-18-3]
(2) Tributylphosphate; C₁₂H₂₇O₄P; [126-73-8]

ORIGINAL MEASUREMENTS:

VARIABLES:
T/K = 298

PREPARED BY:
T. Mioduski and M. Salomon

EXPERIMENTAL VALUES:

<table>
<thead>
<tr>
<th>mass %</th>
<th>mol/kg sln</th>
<th>g dm⁻³</th>
<th>mol dm⁻³</th>
<th>mol kg⁻¹ (compilers)</th>
<th>density/g cm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>41.4</td>
<td>1.49</td>
<td>580.2</td>
<td>2.03</td>
<td>2.57</td>
<td>1.40</td>
</tr>
</tbody>
</table>

The solid phase is TmCl₃

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Saturated solutions prepared isothermally with magnetic stirring. Equilibrium was attained after 25-30 d. The solution was centrifuged and an aliquot for analysis taken and added to methanol and precipitated with aq NH₃. The pptd Tm(OH)₃ was washed repeatedly and heated to the oxide for gravimetric analysis. The solid phase was analyzed (no details given) for phosphorous, and only the anhydrous TmCl₃ was found.

All operations were performed in a dry box through which a stream of argon was passed.

The major objective of this work was to establish the nature of complexation between TBP and TmCl₃ in solution.

SOURCE AND PURITY OF MATERIALS:
Anhydrous TmCl₃ prepared by chlorination of the oxide with CCl₄ vapor (1,2). Source and purity of materials not given. Tm was analyzed gravimetrically, and Cl by Volhard's method.

Tributylphosphate (TBP) was purified "by the standard method." No additional details given.

ESTIMATED ERROR:
No estimate possible.

REFERENCES:
COMPONENTS:
(1) Thulium chloride; TmCl₃; [13537-18-3]
(2) Amines

ORIGINAL MEASUREMENTS:
Kirmse, E.M.
Tř. II Vesl. Koně, po Teor. Rastvorov
1971, 200-6.

VARIABLES:
T/K = 298

PREPARED BY:
T. Mioduski and M. Salomon

EXPERIMENTAL VALUES:

<table>
<thead>
<tr>
<th>Solvent</th>
<th>solubilityᵃ</th>
<th>mass %</th>
<th>mol kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-propanamine;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-propen-1-amine;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃H₇N; [107-11-9]</td>
<td>29.0</td>
<td>1.484</td>
<td></td>
</tr>
<tr>
<td>iso-C₃H₉N; [75-31-0]</td>
<td>13.7</td>
<td>0.577</td>
<td></td>
</tr>
</tbody>
</table>

ᵃMolalities calculated by the compilers.

ᵇThe original paper simply specifies the solvent as C₃H₅NH₂, and upon request, the author kindly identified the solvent as allylamine.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Experimental details not given, but were probably similar to previous works of the author which are compiled throughout this volume.

SOURCE AND PURITY OF MATERIALS:
Nothing specified, but based on previous work by the author, the anhydrous salt was probably prepared by the method of Taylor and Carter (1).

ESTIMATED ERROR:
Nothing specified.

REFERENCES:
1. Taylor, M.D.; Carter, C.P.
**COMPONENTS:**

1. Thulium chloride; TmCl₃; [13537-18-3]
2. Hexamethylphosphorotriamide; C₆H₁₈N₃O₃P; [680-31-9]

**ORIGINAL MEASUREMENTS:**

Mikheev, N.B.; Kamenskaya, A.N.; Konovalova, N.A.; Zhilina, T.A.


**VARIABLES:**

Room temperature: \( T/K = 298 \pm 3 \)

**EXPERIMENTAL VALUES:**

Starting with the solvate \( \text{TmCl}_3 \cdot 3((\text{CH}_3)_2\text{N})_3\text{PO} \), the solubility at 25 ± 3°C was given as

\[
0.0935 \text{ mol dm}^{-3}
\]

\( ^a \) Table 3 in the English translation of the source paper states the temperature to be 23 ± 3°C. This is probably a typographical error as the text clearly states that all measurements were carried out at 25 ± 3°C.

**PREPARED BY:**

T. Mioduski and M. Salomon

**AUXILIARY INFORMATION**

**METHOD/APPARATUS/PROCEDURE:**

Isothermal method. Salt and solvent were placed in a test-tube in a dry box, and the tube agitated at room temperature until equilibrium was reached. Aliquots were withdrawn periodically and analyzed for the metal content. Rare earth concentration was determined by complexometric titration, and by the radiometric method using the isotope \( \text{Tm}^{170} \) (\( t_{1/2} = 169 \text{ d} \)). Authors state that results for both methods agreed. Although not clearly stated, it appears that equilibrium was reached in several weeks to several months.

Solid phase samples washed three times with benzene or ether and dried on a steam bath in an argon atmosphere. The solid phase was analyzed and found to be \( \text{TmCl}_3 \cdot 3((\text{CH}_3)_2\text{N})_3\text{PO} \).

The solvate was analyzed for metal content by complexometric titration, for chloride by the Volhard method, and the solvent was obtained by difference. IR spectra confirmed the absence of water. Structural studies of the solvate were also carried out by X-ray analysis.

**SOURCE AND PURITY OF MATERIALS:**

Anhydrous TmCl₃, prepared by modification of Taylor and Carter's method (1) by subliming \( \text{NH}_4\text{Cl} \) from a mixture of TmCl₃ with 6 moles of \( \text{NH}_4\text{Cl} \) in a stream of inert gas at 200-400°C. The product contained less than 3% of \( \text{TmOCl} \).

The solvent was purified as in (2).

**ESTIMATED ERROR:**

Soly: precision ± 0.001 mol dm⁻³ at a 95% level of confidence (authors).

Temp: precision ± 3K.

**REFERENCES:**

COMPONENTS:
(1) Thulium chloride; TmCl₃; [13537-18-3]
(2) Tetrachlorostannate; SnCl₄; [7646-78-8]
(3) Phosphorus oxychloride; POCl₃; [10025-87-3]

VARIABLES:
T/K = 293
Concentration of SnCl₄

EXPERIMENTAL VALUES:

<table>
<thead>
<tr>
<th>SnCl₄:POCl₃ ratio (by volume)</th>
<th>SnCl₄ concentration mol dm⁻³</th>
<th>Tm₂O₃ solubilitya,b moles Tm dm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:100</td>
<td>0.085</td>
<td>0.8</td>
</tr>
<tr>
<td>1:50</td>
<td>0.17</td>
<td>0.8 (0.6)</td>
</tr>
<tr>
<td>1:25</td>
<td>0.33</td>
<td>1.2</td>
</tr>
<tr>
<td>1:15</td>
<td>0.59</td>
<td>1.3</td>
</tr>
<tr>
<td>1:10</td>
<td>0.78</td>
<td>2.1</td>
</tr>
</tbody>
</table>

a This is also the solubility of TmCl₃ in the SnCl₄-POCl₃ mixtures because the oxide is quantitatively converted to the chloride according to:

Tm₂O₃ + 6POCl₃ = 2TmCl₃ + 3P₂O₃Cl₄

Thus the equilibrated solutions should actually be considered to be a four component system containing SnCl₄, TmCl₃, P₂O₃Cl₄ and POCl₃ (the compiler assumes P₂O₃Cl₄ is soluble).

b Mixtures preheated to 220°C for 2 hours prior to equilibration at 20°C (value in parenthesis indicates preheating at 120°C.)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Isothermal method used. POCl₃ + SnCl₄ solutions were prepared by volume in a dry box. The SnCl₄ content was verified by chemical analysis for Sn. This solution and Tm₂O₃ were placed in sealed ampoules, heated to 20-250°C to increase the rate of solution, and then rotated in an air thermostat at 20°C for 2-200 hours. Without preheating, equilibrium was established after 200 hours. Preheating to 220°C lowered the equilibration time at 20°C to 2 hours.

Tm was determined by colorimetric analysis, and in some cases by the oxalate method. The reported solubilities are mean values based on 3-5 parallel determinations.

SOURCE AND PURITY OF MATERIALS:
Tm₂O₃ of "the first sort" was heated at 950°C for 2 hours.
"Pure" grade SnCl₄ and POCl₃ were dehydrated with P₂O₅ and distilled under vacuum.

ESTIMATED ERROR:
Soly: authors state the "coefficient of variance" to be less than 7%.
Temp: precision presumably ± 0.2K (compiler).

REFERENCES: