| COMPONENTS: | ORIGINAL MEASUREMENTS: |
|---|---|
| (1) Thulium chloride; $TmCl_3$; [13537-18-3]<br>(2) Ethanol; $C_2H_6O$; [64-17-5]<br>(3) Water; $H_2O$; [7732-18-5] | Sakharova, Yu.G.; Ezhova, T.A.<br>*Zh. Neorg. Khim.* 1976, *21*, 551-4; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1976, *21*, 296-8. |
| VARIABLES:<br>Temperature | PREPARED BY:<br>T. Mioduski and M. Salomon |

EXPERIMENTAL VALUES:

solubility of $TmCl_3.6H_2O$ in 96.8% $C_2H_5OH$[a]

| | sample 1 | sample 2 | sample 3 | sample 4 | mean solubilities | |
|---|---|---|---|---|---|---|
| t/°C | g/100 g[b] | g/100 g | g/100 g | g/100 g | g/100 g | mol $kg^{-1}$[c] |
| 20 | 42.09 | 42.20 | 42.26 | 41.91 | 42.11 | 1.897 |
| 30 | 41.06 | 41.16 | 41.12 | 41.14 | 41.11 | 1.821 |
| 40 | 41.70 | 41.73 | 42.09 | 41.83 | 41.83 | 1.876 |
| 50 | 41.17 | 44.21 | 44.44 | 44.50 | 44.33 | 2.077 |
| 60 | 47.08 | 47.26 | 47.46 | 47.35 | 47.29 | 2.340 |

[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: | SOURCE AND PURITY OF MATERIALS: |
|---|---|
| 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.<br><br>The metal content in each aliquot taken for analysis was determined by complexometric titration with Trilon B.<br><br>Analyses of the solids withdrawn at 20°C, 40°C and 60°C showed the solid phase to be the hexahydrate: i.e. ethanol was not found in any of the solid phases. | $TmCl_3.6H_2O$ 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 $CaCl_2$, $P_2O_5$ and NaOH. The crystals analyzed for the metal by titrn 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 $CuSO_4$ followed by distn. Ethanol concn detd refractometrically and pycnometrically. |
| | ESTIMATED ERROR:<br>Soly: results apparently precise to within ± 0.9 % (compilers).<br>Temp: nothing specified. |
| | REFERENCES: |

| COMPONENTS: | ORIGINAL MEASUREMENTS: |
|---|---|
| (1) Thulium chloride; $TmCl_3$; [13537-18-3]<br>(2) 2-Methoxyethanol; $C_3H_8O_2$; [109-86-4] | Kirmse, E.M.<br>*Tr. II Vses. Konf. po Teor. Rastvorov* 1971, 200-6. |
| **VARIABLES:**<br>T/K = 298 | **PREPARED BY:**<br>T. Mioduski |

**EXPERIMENTAL VALUES:**

The solubility of $TmCl_3$ 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.

**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. *J. Inorg. Nucl. Chem.* 1962, *24*, 387.

| COMPONENTS: | ORIGINAL MEASUREMENTS: |
|---|---|
| (1) Thulium chloride; $TmCl_3$; [13537-18-3]<br><br>(2) Diethyl ether; $C_4H_{10}O$; [60-29-7] | Dzhuraev, Kh. Sh.; Mirsaidov, U.; Kurbanbekov, A.; Rakhimova, A.<br><br>*Dokl. Akad. Nauk Tadzh. SSR* 1976, *19*, 32-4 |
| **VARIABLES:** | **PREPARED BY:** |
| T/K = 293 | T. Mioduski |

**EXPERIMENTAL VALUES:**

The solubility of $TmCl_3$ in diethyl ether at 20°C was reported as

0.053 mass %

The corresponding molality calculated by the compiler is

$1.94 \times 10^{-3}$ mol $kg^{-1}$

**AUXILIARY INFORMATION**

| METHOD/APPARATUS/PROCEDURE: | SOURCE AND PURITY OF MATERIALS: |
|---|---|
| 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 $AgNO_3$. The solid phase corresponded to $TmCl_3.Et_2O$ (the etherate was dried under vaccum at 40°C prior to analysis). | Anhydrous $TmCl_3$ prepared by the ethanol solvate method (no details given).<br><br>Ethyl ether was dried with Na and distilled from $LiAlH_4$. |
| | **ESTIMATED ERROR:**<br>Nothing specified. |
| | **REFERENCES:** |

| COMPONENTS: | ORIGINAL MEASUREMENTS: |
|---|---|
| (1) Thulium chloride; $TmCl_3$; [13537-18-3]<br>(2) 1,2-Diethoxyethane; $C_6H_{14}O_2$; [629-14-1] | Kirmse, E.M.; Zwietasch, K.J.<br>*Z. Chem.* 1967, *7*, 281. |
| VARIABLES:<br>T/K = 298 | PREPARED BY:<br>T. Mioduski |

EXPERIMENTAL VALUES:

The solubility of $TmCl_3$ in 1,2-diethoxyethane at 25°C was reported to be

0.88 mass %

The corresponding molality calculated by the compiler is

$0.0323 \text{ mol kg}^{-1}$

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: | SOURCE AND PURITY OF MATERIALS: |
|---|---|
| Isothermal method used. The anhydrous mixtures were equilibrated at 25°C for several days with frequent shaking.<br><br>The solid phase was dried in a vacuum desiccator over $P_2O_5$.<br><br>Tm was determined by complexometric titration using Xylenol Orange indicator. Chloride was determined by the Volhard titration method. | Sources and purities of materials not given. The anhydrous chloride was obtained by the method of Taylor and Carter (1).<br><br>The solvent was prepared by the Williamson synthesis: i.e. by reaction of $C_2H_5I$ with the monoethylether of ethylene glycol. |
| | ESTIMATED ERROR:<br>No estimates possible. |
| | REFERENCES:<br>1. Taylor, M.D.; Carter, C.P. *J. Inorg. Nucl. Chem.* 1962, *24*, 387. |

| COMPONENTS: | ORIGINAL MEASUREMENTS: |
|---|---|
| (1) Thulium chloride; $TmCl_3$; [13537-18-3] | Korovin, S.S.; Galaktionova, O.V.; Lebedeva, E.N.; Voronskaya, G.N. |
| (2) Tributylphosphate; $C_{12}H_{27}O_4P$; [126-73-8] | *Zh. Neorg. Khim.* 1975, *20*, 908-14; *Russ. J. Inorg. Chem.* (*Engl. Transl.*) 1975, *20*, 508-11. |
| **VARIABLES:** | **PREPARED BY:** |
| T/K = 298 | T. Mioduski and M. Salomon |

**EXPERIMENTAL VALUES:**

Composition of saturated solutions

| mass % | mol/kg sln | g $dm^{-3}$ | mol $dm^{-3}$ | mol $kg^{-1}$ (compilers) | density/g $cm^{-3}$ |
|---|---|---|---|---|---|
| 41.4 | 1.49 | 580.2 | 2.03 | 2.57 | 1.40 |

The solid phase is $TmCl_3$

**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 $NH_3$. 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 $TmCl_3$ 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 $TmCl_3$ in solution.

**SOURCE AND PURITY OF MATERIALS:**

Anhydrous $TmCl_3$ prepared by chlorination of the oxide with $CCl_4$ 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:**

1. Korshunov, B.G.; Drobot, D.V.; Bukhtiyarov, V.V.; Shevtsova, Z.N. *Zh. Neorg. Khim.* 1964, *9*, 1427.

2. Novikov, G.I.; Tolmacheva, V.D. *Zh. Prikl. Khim.* 1965, *38*, 1160.

| COMPONENTS: | ORIGINAL MEASUREMENTS: |
|---|---|
| (1) Thulium chloride; $TmCl_3$; [13537-18-3]<br>(2) Amines | Kirmse, E.M.<br>*Tr. II Vses. Konf. po Teor. Rastvorov* 1971, 200-6. |
| **VARIABLES:**<br>T/K = 298 | **PREPARED BY:**<br>T. Mioduski and M. Salomon |

**EXPERIMENTAL VALUES:**

| solvent | | | solubility[a] mass % | mol $kg^{-1}$ |
|---|---|---|---|---|
| 2-propanamine; | iso-$C_3H_9N$; | [75-31-0] | 13.7 | 0.577 |
| 2-propen-1-amine;[b] | $C_3H_7N$; | [107-11-9] | 29.0 | 1.484 |

[a]Molalities calculated by the compilers.

[b]The original paper simply specifies the solvent as $C_3H_5NH_2$, 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.

Nature of solid phases not specified.

**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.
*J. Inorg. Nucl. Chem.* 1962, *24*, 387.

| COMPONENTS: | ORIGINAL MEASUREMENTS: |
|---|---|
| (1) Thulium chloride; $TmCl_3$; [13537-18-3]<br>(2) Hexamethylphosphorotriamide; $C_6H_{18}N_3OP$; [680-31-9] | Mikheev, N.B.; Kamenskaya, A.N.; Konovalova, N.A.; Zhilina, T.A.<br>*Zh. Neorg. Khim.* 1977, *22*, 1761-6; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1977, *22*, 955-8. |
| **VARIABLES:**<br>Room temperature: T/K = 298 ± 3 | **PREPARED BY:**<br>T. Mioduski and M. Salomon |

**EXPERIMENTAL VALUES:**

Starting with the solvate $TmCl_3.3((CH_3)_2N)_3PO$, the solubility at 25 ± 3°C[a] 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.

**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 Tm 170 ($t_{1/2}$ = 169 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 $TmCl_3.3C_6H_{18}N_3OP$.

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 $TmCl_3$, prepared by modification of Taylor and Carter's method (1) by subliming $NH_4Cl$ from a mixture of $TmCl_3$ with 6 moles of $NH_4Cl$ in a stream of inert gas at 200-400°C. The product contained less than 3% of 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:**

1. Taylor, M.D.; Carter, C.P. *J. Inorg. Nucl. Chem.* 1962, *24*, 387.
2. Fomicheva, M.G.; Kessler, Yu.M.; Zabusova, S.E.; Alpatova, N.M. *Elektrokhimiya* 1975, *11*, 163.

| COMPONENTS: | ORIGINAL MEASUREMENTS: |
|---|---|
| (1) Thulium chloride; $TmCl_3$; [13537-18-3]<br>(2) Tetrachlorostannate; $SnCl_4$; [7646-78-8]<br>(3) Phosphorus oxychloride; $POCl_3$; [10025-87-3] | Lyubimov, E.I.; Batyaev, I.M.<br>*Zh. Prikl. Khim.* 1972, *45*, 1176-8. |
| **VARIABLES:**<br>T/K = 293<br>Concentration of $SnCl_4$ | **PREPARED BY:**<br>T. Mioduski |

**EXPERIMENTAL VALUES:**

| $SnCl_4$:$POCl_3$ ratio (by volume) | $SnCl_4$ concentration mol $dm^{-3}$ | $Tm_2O_3$ solubility[a,b] moles Tm $dm^{-3}$ |
|---|---|---|
| 1:100 | 0.085 | 0.8 |
| 1:50 | 0.17 | 0.8 (0.6) |
| 1:25 | 0.33 | 1.2 |
| 1:15 | 0.59 | 1.3 |
| 1:10 | 0.78 | 2.1 |

[a]This is also the solubility of $TmCl_3$ in the $SnCl_4$-$POCl_3$ mixtures because the oxide is quantitatively converted to the chloride according to

$$Tm_2O_3 + 6POCl_3 = 2TmCl_3 + 3P_2O_3Cl_4$$

Thus the equilibrated solutions should actually be considered to be a four component system containing $SnCl_4$, $TmCl_3$, $P_2O_3Cl_4$ and $POCl_3$ (the compiler assumes $P_2O_3Cl_4$ 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. $POCl_3$ + $SnCl_4$ solutions were prepared by volume in a dry box. The $SnCl_4$ content was verified by chemical analysis for Sn. This solution and $Tm_2O_3$ 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° 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:**

$Tm_2O_3$ of "the first sort" was heated at 950°C for 2 hours.

"Pure" grade $SnCl_4$ and $POCl_3$ were dehydrated with $P_2O_5$ 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:**