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## PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

# Solubility in the $PrCl_3$–$SmCl_3$–HCl–$H_2O$ System at 25°C

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**Abstract**—The solubility in the $PrCl_3$–$SmCl_3$–HCl– $H_2O$ quaternary water–salt system was studied at 25°C along the 40% hydrochloric acid section (a system with solid solutions and discontinuity). The composition of the discontinuity point was as follows: $PrCl_3 \cdot 7H_2O$, 2.33; $SmCl_3 \cdot 6H_2O$, 0.11; HCl, 40.05; and $H_2O$, 57.51 wt %.

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This work continues our studies of phase equilibria in $LnCl_3$–$Ln'Cl_3$–HCl–$H_2O$ systems [1, 2]. The difference between the solubilities of individual rare-earth metal chlorides increases with the hydrochloric acid concentration [3]. The ion radius and crystal structure of the salt (dimer, monomer) also affect the solubility of lanthanide chlorides [4]. Solubility was studied in the $PrCl_3$–$SmCl_3$–$H_2O$ system including lanthanide chlorides with similar ion radii and different crystal structures [5]. We studied solubility in the $PrCl_3$–$SmCl_3$–HCl–$H_2O$ system at 25°C along the 40% HCl section to evaluate the influence of the hydrochloric acid concentration on the character of the evolved phases.

## EXPERIMENTAL

Solubility was studied by the method described in [6–8], determining the solvent concentration in equilibrium liquid phases as a function of the salt composition of initial mixtures lying on the sections with a constant percentage of some component.

Praseodymium and samarium chlorides were synthesized as follows. A solution of oxalic acid was added in a 50% excess over stoichiometry to a solution of a rare-earth metal nitrate (chemically pure grade). The oxalate precipitate was washed with distilled water, filtered off, dried, and calcined at 950°C for 2 h. The resulting oxide was dissolved in hydrochloric acid. The rare-earth metal chloride was dried to a constant weight at a temperature that excluded the loss of water of crystallization. The water of crystallization was determined by the weight loss on the ignition of $PrCl_3 \cdot 7H_2O$ and $SmCl_3 \cdot 6H_2O$ to oxychlorides at 500 and 380°C, respectively.

The isothermic medium was maintained in a TZh-TS-01 water thermostat with an accuracy of ±0.1°C. Thermodynamic equilibrium in the system was established in 4 h with continuous stirring.

The system was studied along the section passing through the figurative points of $PrCl_3 \cdot 7H_2O$ and $SmCl_3 \cdot 6H_2O$ and the point corresponding to 40 wt % HCl. $PrCl_3 \cdot 7H_2O$ and $SmCl_3 \cdot 6H_2O$ begin to lose water of crystallization at 40 and 70°C, respectively [9]. Based on this fact, equilibrium liquid phases were brought to a constant weight at a temperature not higher than 40°C to retain the constant composition of the praseodymium and samarium crystal hydrates.

The solvent in the equilibrium liquid phases was determined along the 90 and 95 wt % (HCl + $H_2O$) sections. The functional curves showing the dependence of the solvent percentage in the equilibrium liquid phases on the salt composition of the initial mixtures arranged along sections with the constant $\Sigma$(HCl + $H_2O$) content are presented in Fig. 1. The shape of these curves and

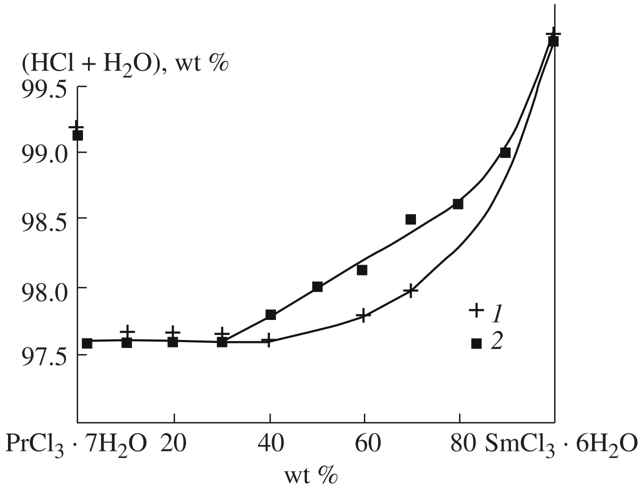

**Fig. 1.** HCl + $H_2O$ content in equilibrium liquid phases vs. the salt composition of the initial mixtures along the (*1*) 90 and (*2*) 95 wt % $\Sigma$($H_2O$ + HCl) sections at 25°C.

Compositions of equilibrium phases in the $PrCl_3$–$SmCl_3$–HCl–$H_2O$ system at 25°C

| Composition of liquid phase, wt % | | | | Composition of solid phase, wt % | | $K_{Pr/Sm}$ |
|---|---|---|---|---|---|---|
| $PrCl_3 \cdot 7H_2O$ | $SmCl_3 \cdot 6H_2O$ | HCl | $H_2O$ | $PrCl_3 \cdot 7H_2O$ | $SmCl_3 \cdot 6H_2O$ | |
| 0.85 | 0 | 40.70 | 58.45 | 100 | 0 | |
| 2.46 | 0.06 | 40.02 | 57.46 | 87.69 | 12.31 | 5.76 |
| 2.42 | 0.08 | 40.02 | 57.48 | 83.54 | 16.46 | 5.96 |
| 2.31 | 0.1 | 40.06 | 57.53 | 75.47 | 24.53 | 7.51 |
| 2.29 | 0.12 | 40.06 | 57.53 | 66.72 | 33.28 | 9.52 |
| 2.27 | 0.13 | 40.06 | 57.54 | 63.02 | 36.98 | 10.25 |
| 2.23 | 0.18 | 40.06 | 57.53 | 50.08 | 49.92 | 12.35 |
| 1.94 | 0.26 | 40.15 | 57.65 | 39.13 | 60.87 | 11.61 |
| 1.77 | 0.23 | 40.23 | 57.77 | 25.75 | 74.25 | 22.19 |
| 1.67 | 0.35 | 40.22 | 57.76 | 18.01 | 81.99 | 21.72 |
| 1.18 | 0.32 | 40.43 | 58.07 | 10.05 | 89.95 | 33.00 |
| 0.93 | 0.47 | 40.48 | 58.12 | 2.62 | 97.38 | 73.54 |
| 0.51 | 0.49 | 40.64 | 58.36 | 0.26 | 99.74 | 400.00 |
| 0 | 0.17 | 40.98 | 58.85 | 0 | 100 | |

the tie-lines derived indicate that the $PrCl_3$–$SmCl_3$–HCl–$H_2O$ system is a type IV solid solution (with discontinuity). To confirm this, we determined praseodymium and samarium in the liquid phases by atomic emission on a Shimadzu ICPE 9000 spectrometer.

To determine the compositions of solid phases, we used the tie-line equation passing through the initial composition and the liquid and solid phases equilibrated with the initial composition:

$$\frac{x_s - x_l}{x_i - x_l} = \frac{y_s - y_l}{y_i - y_l} = \frac{z_s - z_l}{z_i - z_l},$$

where $x$, $y$, and $z$ are the concentrations of the relevant components.

The averaged composition of the discontinuity point is as follows (wt %): $PrCl_3 \cdot 7H_2O$, 2.33; $SmCl_3 \cdot 6H_2O$, 0.11; HCl, 40.05; and $H_2O$, 57.51.

The compositions of the equilibrium phases are presented in the table and in Fig. 2.

Solid solutions of the **IV** type are also formed in the $PrCl_3$–$SmCl_3$–$H_2O$ system, and the discontinuity point has the following composition (wt %): $PrCl_3 \cdot 7H_2O$, 54.87; $SmCl_3 \cdot 6H_2O$, 18.77; and $H_2O$, 26.35 [5]. Thus, with an increase in the hydrochloric acid concentration to 40 wt %, the discontinuity point shifts to the lateral side of the $PrCl_3$–HCl–$H_2O$ concentration tetrahedron. The crystallization field of solid solutions based on $SmCl_3 \cdot 6H_2O$ increases, and the solid phases are considerably enriched in samarium. The separation coefficients of praseodymium and samarium chlorides are listed in the table. These values are higher by one order of magnitude than analogous data for an aqueous system [5], especially in the region of low and medium samarium concentrations.

The line of saturated solutions was approximated by a second-degree polynomial using the least-squares method $3598.5669x^2 + 8.1417 \times 10^4 y^2 + 2.6451 \times 10^4 xy - 130.6725x - 633.8311y + 1 = 0$, (with variance of $1.29 \times 10^{-1}$), where $x$ is the $PrCl_3 \cdot 7H_2O$ concentration and $y$ is the $SmCl_3 \cdot 6H_2O$ concentration.

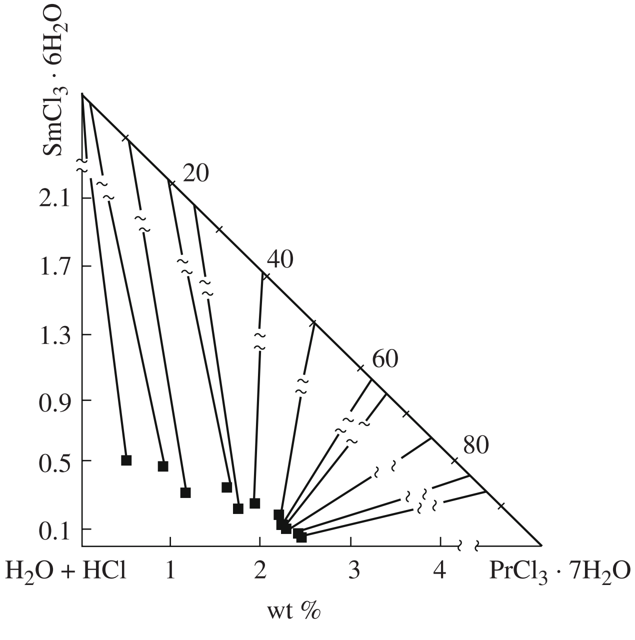

**Fig. 2.** Solubility isotherm of the $PrCl_3$–$SmCl_3$–HCl–$H_2O$ system at 25°C.

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