

C. GUMIŃSKI*

PHASE DIAGRAMS OF THE WATER-RICH PARTS OF THE RARE EARTH METAL CHLORIDE – WATER SYSTEMS

DIAGRAMY FAZOWE CZĘŚCI BOGATYCH W WODĘ DLA UKŁADÓW CHLOROK METALU ZIEMI RZADKIEJ – WODA

Literature data related to the solubility and phase diagrams of the aqueous binary and ternary systems containing rare earth metal chlorides are collected and presented in a condensed form. A comparison of the binary phase diagram shapes of the water-rich parts showed quite smooth changes of their invariant points and temperature ranges of stability of the equilibrium solid phases. Such regularities allowed to predict the $\text{PmCl}_3\text{-H}_2\text{O}$, $\text{HoCl}_3\text{-H}_2\text{O}$ and $\text{TmCl}_3\text{-H}_2\text{O}$ phase diagrams which were earlier not investigated by experiments. Some similarities were observed in case of aqueous ternary systems containing rare earth metal chloride and various inorganic and organic salts as well as non-electrolyte organic compounds; the complex compound formations of rare earth metal chlorides with chlorides of Cs, Cd or Zn, and with trimethylamine hydrochloride or urea were presented as examples.

Keywords: solubility of rare earth metal chlorides in aqueous systems, phase diagrams of the $\text{PmCl}_3\text{-H}_2\text{O}$, $\text{HoCl}_3\text{-H}_2\text{O}$ and $\text{TmCl}_3\text{-H}_2\text{O}$ systems

Dane literaturowe dotyczące rozpuszczalności i diagramów fazowych układów podwójnych i potrójnych zawierających wodę i chlorki metali ziem rzadkich zostały przedstawione w formie syntetycznej. Punkty charakterystyczne i temperaturowe zakresy stabilności równowagowych faz stałych dla części diagramów bogatych w wodę wykazują stopniowe zmiany w szeregu tych metali. Te regularności pozwoliły przewidzieć diagramy fazowe dla układów $\text{PmCl}_3\text{-H}_2\text{O}$, $\text{HoCl}_3\text{-H}_2\text{O}$ i $\text{TmCl}_3\text{-H}_2\text{O}$, które nie były wcześniej badane eksperymentalnie. Zaobserwowano pewne podobieństwa w przypadku układów potrójnych zawierających chlorki metali ziem rzadkich, różne nieorganiczne i organiczne sole, oraz związki organiczne nie będące elektrolitami; jako przykładów użyto tworzenia się związków kompleksowych chlorków metali ziem rzadkich z chlorkami Cs, Cd lub Zn, chlorowodorkiem trimetyloaminy lub mocznikiem.

1. Introduction

Chlorides of rare earth metals (RECl_3) have many significant applications in technology and science. They are used as catalysts in organic synthesis and polymerization, for production of important alloys and compounds, lighting (luminescence) materials, in nuclear fuel reprocessing as well as they are used as dyes for glass and ceramics. Therefore investigations of the solubility equilibria and corresponding phase diagrams are essential for the mentioned applications as well as for knowledge of the quantitative solubility data, identification of complex compounds formed in multi-component systems (double salts, complexes, solid solutions of hydrates) and improvement of extraction and refining of rare earth metals.

The material related to the phase diagrams and solubility data of the rare earth metal chloride – water systems was not previously evaluat-

ed in the literature. The information relevant to the binary ($\text{RECl}_3\text{-H}_2\text{O}$), ternary ($\text{RECl}_3\text{-acid-H}_2\text{O}$, $\text{RECl}_3\text{-salt-H}_2\text{O}$, $\text{RECl}_3\text{-organics-H}_2\text{O}$) and quarternary ($\text{RECl}_3\text{-salt-salt-H}_2\text{O}$, $\text{RECl}_3\text{-acid-salt-H}_2\text{O}$) systems make ~20, ~70 and ~10% of the literature sources, respectively. The corresponding results were collected, systematically evaluated, selected and will be published in details in a monograph [1]. In this paper we outline only the most important aspects of this assessment procedure, present typical examples, point on some similarities and distinctnesses of these systems.

2. Solubility results

As an example of the evaluation procedure we present the solubility data of YCl_3 in H_2O over the wide temperature range of 231–653 K. The all corresponding values from 17 papers are shown in Fig. 1 as logarithm

* DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WARSAW 02-093 WARSZAWA, 1 PASTEURA STR., POLAND

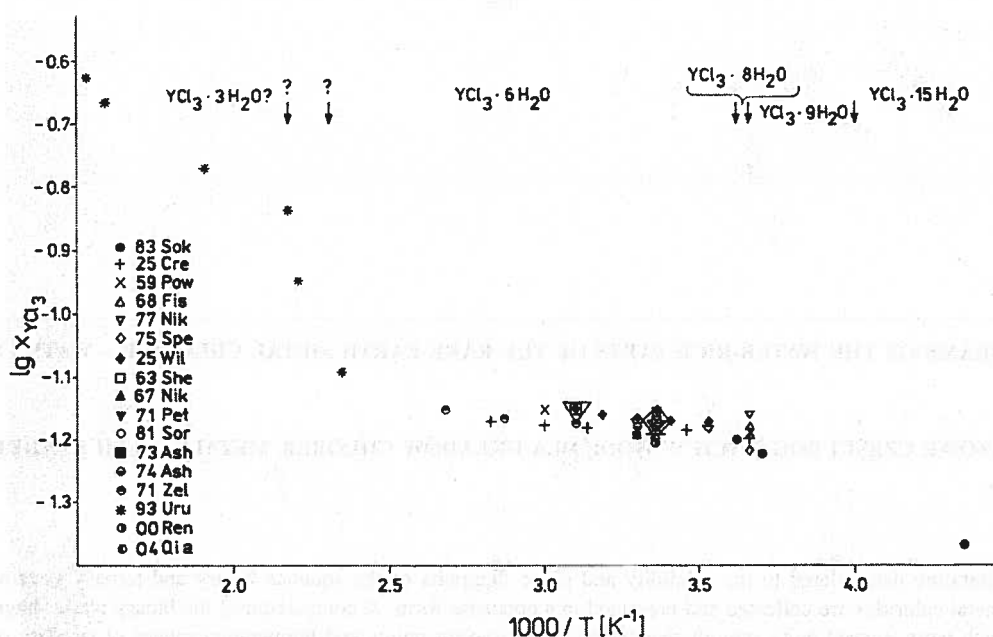


Fig. 1. Temperature dependence of the solubility of YCl_3 in water

25Cre: M.C. Crew et al., *J. Phys. Chem.* **29**, 34 (1925); 25Wil: M.D. Williams et al., *J. Am. Chem. Soc.* **47**, 297 (1925); 59Pow: J.E. Powell, *U.S. Atom. Ener. Comm. Rep. IS-15*, p. 10 (1959); 63She: Z.N. Shevtsova et al., *Zh. Neorg. Khim.* **8**, 1749 (1963); 67Nik: A.V. Nikolaev et al., *Dokl. Akad. Nauk SSSR* **172**, 1333 (1967); 68Fis: W. Fischer, *Z. Anorg. Chem.* **357**, 177 (1968); 71Pet: V.S. Petelina et al., *Issled. Obl. Khim. Redkozemel. Elem.* **3**, 48 (1971); 71Zel: A.N. Zelikman et al., *Zh. Neorg. Khim.* **16**, 2023 (1971); 73Ash: G.A. Ashimkulova et al., *Zh. Neorg. Khim.* **18**, 2011 (1973); 74Ash: G.A. Ashimkulova et al., *Zh. Neorg. Khim.* **19**, 2588 (1974); 75Spe: F.H. Spedding et al. *J. Chem. Eng. Data* **20**, 72 (1975) & **21**, 341 (1976); 77Nik: A.V. Nikolaev et al., *Izv. Sibir. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **1977**, no 4, 84; 81Sor: A.A. Sorokina et al., *Izv. Sibir. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **1981**, no 5, 51; 83Sok: N.P. Sokolova, *Zh. Neorg. Khim.* **28**, 782 (1983); 93Uru: M.A. Urusova, *Zh. Neorg. Khim.* **38**, 1074 (1993); 00Ren: F. Ren et al., *Yingyong Huaxue (Chinese J. Appl. Chem.)* **17**, 203 (2000); 04Qia: Zh.P. Qiao et al., *Wuji Huaxue Xuebao (Chinese J. Inorg. Chem.)* **20**, 929 (2004)

of the solubility versus reciprocal temperature. One may easily observe that the data are significantly scattered and the line drawn through the mean results display a quite irregular dependence. Only the results of 75Spe were reported to be precise within $\pm 0.1\%$ and of 04Qia within $\pm 0.2\%$ (at the best). Precision of the rest of the results was between ± 1 and $\pm 3\%$, but most frequently it was not specified. Therefore one should be very careful with half-baked interpretations of any inflexions observed on the solubility curve shown in Fig. 1. The breaks may be, as well as may be not, connected with the peritectic reactions occurring in the binary $\text{YCl}_3\text{-H}_2\text{O}$ system. Any rational interpretation of the solubility dependence would be impossible without knowledge of the $\text{YCl}_3\text{-H}_2\text{O}$ phase diagram. Another complication in the evaluation is a tendency of the system to immiscibility what is manifested by the strong curvature of the solubility dependence between 373 and 458 K.

The arrows in the upper part of the Fig. 1 denote peritectic temperatures for the $\text{YCl}_3\text{-H}_2\text{O}$ system determined by Sokolova [2] by means of thermal anal-

ysis. The following solid phases were found to be in equilibrium with the saturated solutions: $\text{YCl}_3\cdot 15\text{H}_2\text{O}$ (231–250 K), $\text{YCl}_3\cdot 9\text{H}_2\text{O}$ (250–273 K), $\text{YCl}_3\cdot 8\text{H}_2\text{O}$ (273–276 K), $\text{YCl}_3\cdot 6\text{H}_2\text{O}$ (276–458[?] K) and most probably $\text{YCl}_3\cdot 3\text{H}_2\text{O}$ (>458[?] K). The determined temperature of the peritectic decomposition of $\text{YCl}_3\cdot 6\text{H}_2\text{O}$ reported in several papers was scattered between 426 and 458 K and a selection of the proper value is not simple. Composition of the solid phases in the $\text{YCl}_3\text{-H}_2\text{O}$ system was determined in [2] by the method of Tamman and the composition of $\text{YCl}_3\cdot 6\text{H}_2\text{O}$ was also confirmed by chemical analysis and the (wet residue) method of Schreinemakers during investigations of several ternary systems containing $\text{YCl}_3\cdot 6\text{H}_2\text{O}$. Existence of the equilibrium solid phase $\text{YCl}_3\cdot 3\text{H}_2\text{O}$ at higher temperatures was deduced from the dehydration studies of $\text{YCl}_3\cdot 6\text{H}_2\text{O}$.

Taking into account these facts we should separately analyze the selected parts of the liquidus between the peritectic temperatures for every system. In the case of well soluble salts in polar solvents (as water), which are characterized by non-linear dependences of the loga-

rithm of solubility versus reciprocal temperature, the use of the following smoothing equation was proposed [3]:

$$\ln \{ x^v (1-x)^r (v+r)^{v+r} r^{-r} [1+(v-1)x]^{-(v+r)} \} = A + BT^{-1} + C \ln T + DT \quad (1)$$

where x is the salt solubility in mol fraction, r the number of water molecules in the equilibrium solid phase, v the number of ions produced upon the salt dissolution and T absolute temperature in K. The constants A , B , C and D are obtainable from the fitting procedure when minimum 4 solubility results at various temperatures are known. These constants have thermodynamic meaning and are related to ΔH , ΔS and Δc_p of the salt dissolution process.

TABLE 1
Comparison of the solubility results of EuCl_3 in water (expressed in mol fractions) at several temperatures as determined by experiments (x_{exp}) and calculated (x_{cal}) from Eq. (2); the equilibrium solid phase is $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$

T/K	x_{exp}	References	x_{cal}
258	0.0593	78 Nik	0.0591
263	0.0607*	78 Nik	0.0592
268	0.0593	78Nik	0.0593
273	0.0595	59Pow	0.0595
	0.0598	77Nik	
283	0.0596	77Nik	0.0598
298	0.0603	67Nik	0.0607
	0.0609	71Nik	
	0.0612	59Pow, 77Nik	
298.15	0.06078	74Spe	0.06073
	0.06073	75Spe	
	0.06065	76Spe	
303	0.0617	77Nik	0.0615
323	0.0661*	77Nik	0.0644
333	0.0661	59Pow	0.0662
431	0.083	88Sok	0.0828

* these results were not taken into account for the formulating Eq. (2)
59Pow: J.E. Powell, U.S. Atom. Ener. Comm. Rep. IS-15, (1959); 67Nik: A.V. Nikolaev et al., Izv. Sibir. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk 1967, no 6, 5; 71Nik: A.V. Nikolaev et al. Izv. Sibir. Otd. Akad. Nauk, Ser. Khim. Nauk 1971, no 4, 61; 74Spe: F.H. Spedding et al., J. Chem. Eng. Data 19, 373 (1974); 75Spe: F.H. Spedding et al., J. Chem. Eng. Data 20, 72 (1975); 76Spe: F.H. Spedding et al., J. Chem. Eng. Data 21, 341 (1976); 77Nik: A.V. Nikolaev et al., Izv. Sibir. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk 1977, no 4, 84; 78Nik: A.V. Nikolaev et al., Izv. Sibir. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk 1978, no 1, 46; 88Sok: N.P. Sokolova, Radiokhimiya 30, 435 (1988)

In case of the $\text{EuCl}_3\text{-H}_2\text{O}$ system, where the equilibrium solid phase is $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, the following solubility equation was obtained from the Eq. (1):

$$\ln \{ x^4 (1-x)^6 (4+6)^{4+6} 6^{-6} [1+(4-1)x]^{-(4+6)} \} = 566.38981 + 0.2565111 T^{-1} - 6.667703 \ln T + 0.007805513 T \quad (2)$$

when selected solubility data from the literature [1] were used for the fitting. Such procedure allowed to calculate the recommended solubility data for EuCl_3 in H_2O at any temperature between the corresponding peritectic points of 254 and 429 K; see Table 1.

TABLE 2
The selected solubilities (in mol fractions) of rare earth metal chlorides in water at 298.15 K

ScCl_3	YCl_3	LaCl_3	CeCl_3	PrCl_3	NdCl_3
0.064-0.100	0.067	0.06558	0.064	0.0655	0.0661
PmCl_3	SmCl_3	EuCl_3	GdCl_3	TbCl_3	DyCl_3
(0.064)	0.06155	0.0607	0.0607	0.0604	0.0614
HoCl_3	ErCl_3	TmCl_3	YbCl_3	LuCl_3	
0.0623	0.0638	0.0653	0.0672	0.0691	

The selected solubility data at 298.15 K for chlorides of all rare earth metals in water are collected in Table 2. As it may be easily noticed, the suggested values belong to various classes of their accuracy what is connected with reproducibility of the most precise results. In the case of ScCl_3 the experimental results were very discrepant and without further decisive studies no precise solubility value may be suggested at present. Due to the divergency of the solubility values for the YCl_3 and CeCl_3 , the selected solubilities are unsufficiently precise. The best concordance of the experimental data was observed in the case of LaCl_3 and SmCl_3 , therefore the suggested values are given with the highest precision. The value for PmCl_3 , given in the parenthesis, was obtained by interpolation of the solubility data for NdCl_3 and SmCl_3 . This is additionally explained in Fig. 2 which collects the selected solubility data according to the atomic number of rare earth metals. The sequence of these elements is reciprocal to their trivalent ionic radii. In conformity with this, the element Y should be placed between Dy and Ho and Sc should be placed far away on right from Lu. According to Fig. 2, the equilibrium solid phases of rare earth metal chlorides at 298 K may be divided into two groups: heptahydrates (La, Ce, Pr) and hexahydrates (all other RE). In the first group, it is difficult to ascribe the solubility minimum for CeCl_3 to any specific effect because the solubility data for this salt are less precise than for LaCl_3 and PrCl_3 . In the case of the second group, one may easily observe the parabola-like dependence of the solubility versus atomic number (or the decreasing ionic radius of the RE metal).

If one would extrapolate the metastable solubility data of $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ from higher temperatures to 298 K, one obtains the metastable LaCl_3 solubility value of $\sim 5.2 \text{ mol kg}^{-1}$ which fits quite well to the extrapolated parabola line at the position of La. The parabola-like dependence of the solubility seems to be resultant of contrary effects: the crystal energy of the salts and the hydration energy of the ions. Nevertheless, the solubility of YCl_3 is higher than it could be predicted from the position of Y being between Dy and Ho; such behavior for YCl_3 is not expected because several other salts of Y have similar properties to Dy and Ho. Taking into account the shape of the solubility dependence in Fig. 2, the undefined solubility value for ScCl_3 (Table 1) seems to be rather near to the upper limit of 6.2 mol kg^{-1} if one extends the parabolic dependence to the proper place of ionic radius of Sc (0.75 nm).

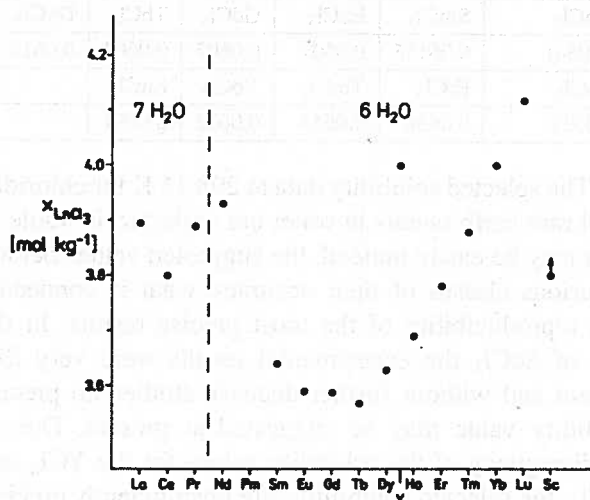


Fig. 2. The selected solubilities of rare earth metal chlorides in water at 298 K

3. Binary phase diagrams

As it was pointed out previously, the phase diagrams of the $\text{RECl}_3\text{-H}_2\text{O}$ systems are fundamental for the solubility evaluation procedure. The only water-rich parts of the diagrams at temperatures lower than 440 K are known so far. Majority of the diagrams was determined with the use of thermal analysis by Sokolova and coworkers [2]. An example of the diagram for the $\text{CeCl}_3\text{-H}_2\text{O}$ system is shown in Fig. 3. Four peritectically formed compounds $\text{CeCl}_3 \cdot 10\text{H}_2\text{O}$, $\text{CeCl}_3 \cdot 9\text{H}_2\text{O}$, $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$ were identified. Temperatures of the peritectic melting of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$ and their crystal structures were also confirmed in other studies [4]. As one may observe in Fig. 3, an addition of CeCl_3 to ice makes a spectacular decrease

of its melting temperature, up to 63 K, what potentially may have practical applications in cooling systems and for the ice melting.

An extension of the investigations of such diagrams to higher temperatures and salt concentrations needs the use of a pressure-resistant apparatus to avoid the solution boiling and water evaporation from the hydrates. Such experiments in a closed system were performed for only the $\text{YCl}_3\text{-H}_2\text{O}$ system by Urusova and Valyashko [5] at temperatures up to 653 K and pressures over 1.3 MPa. There is, however, a general complication of high temperature investigations connected with the hydrolysis reaction of rare earth metal chlorides resulting in the formation of oxychlorides according to the scheme:

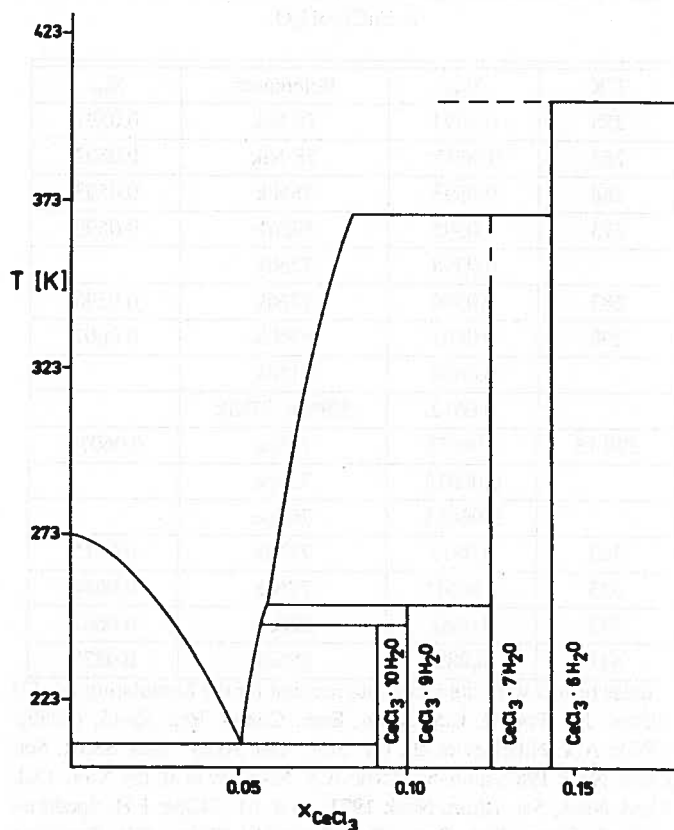
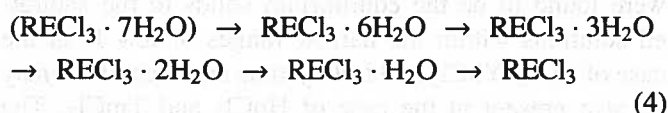


Fig. 3. The partial phase diagram of the $\text{CeCl}_3\text{-H}_2\text{O}$ system obtained from thermal analysis

Advance of such reactions is observable over 370 K and it increases distinctly with temperature. Unfortunately, degree of the advance of the formation of YOCl in the mentioned experiments of [5] was not tested.

Stoichiometry of compounds formed in the salt-richer parts of the phase diagrams may be deduced

from dehydration studies of the hydrates at relatively low temperatures to avoid the hydrolysis. Most of the salts loses water in steps according to the general scheme presented in [6]:



For simplicity of the scheme, the released water molecules were omitted from Eq. (4). In a closed system, the reactions expressed by Eqs. (3) and (4) should be reversible. The Eq. (4) takes into account the reactions proceeding at room and higher temperatures. The last stage, due to the side reaction described by Eq. (3), is the most critical in the dehydration reaction chain but if the process is fast and carefully carried out, the last dehydration step is effective in more than 90%. It is characteristic that no formation of the intermediate hydrates $\text{RECl}_3 \cdot 5\text{H}_2\text{O}$ and $\text{RECl}_3 \cdot 4\text{H}_2\text{O}$ was observed; in fact, these formulae were sometimes proposed but not confirmed in subsequent studies. Thus we can imagine an expansion of the phase diagrams to the more salt-richer parts where $\text{RECl}_3 \cdot 3\text{H}_2\text{O}$, $\text{RECl}_3 \cdot 2\text{H}_2\text{O}$ and $\text{RECl}_3 \cdot \text{H}_2\text{O}$ should be present at the proper places.

The $\text{ScCl}_3\text{-H}_2\text{O}$ system seems to be a special case because only 3 thermal arrests were recorded at 346, 453 and 489 K [7] in the course of thermal analysis. Also $\text{ScCl}_3 \cdot 6\text{H}_2\text{O}$ was observed to dehydrate in a different manner releasing subsequently 2 and 2 molecules of H_2O [7]. Therefore, in connection with a lack of reliable solubility results for ScCl_3 , any sketch of the $\text{ScCl}_3\text{-H}_2\text{O}$ phase diagram would be premature.

Because the all known partial phase diagrams $\text{RECl}_3\text{-H}_2\text{O}$ are similar to the one presented for the $\text{CeCl}_3\text{-H}_2\text{O}$ system in Fig. 3, the characteristic temperatures of these diagrams may be collected in one figure being a kind of the integrated form of 14 phase diagrams known experimentally, what is depicted in Fig. 4. This way, we may analyze the changes of temperature stability ranges of the hydrates formed in the rare earth metal chloride series. The bottom line reflects changes of the eutectic temperatures for these systems. Rather smooth course of these temperatures is disturbed by a jump between GdCl_3 and TbCl_3 . This fact may be explained that the different solid hydrates, namely $\text{GdCl}_3 \cdot 8\text{H}_2\text{O}$ and $\text{TbCl}_3 \cdot 15\text{H}_2\text{O}$, are the equilibrium phases at the corresponding eutectic points. The fields marked above the eutectic line represent the stability ranges (ending at the corresponding peritectic points) of the solid hydrates being in equilibrium with the saturated solutions. We observe that the stoichiometries of the hydrates are characteristic for some groups of the rare earth elements. The most upper line reflects the peritectic decomposition

of the hexahydrates to trihydrates; unfortunately, the formation of trihydrates was not evidentially confirmed in the phase diagram studies so far. This line was drawn through the mean temperature values recorded by [2] and many other investigators [4]. Maximum scatter of these temperatures was within 20 K but typically it was within 10 K. It is a kind of endorsement that the characteristic temperatures reported by [2] are more precise than ± 5 K.

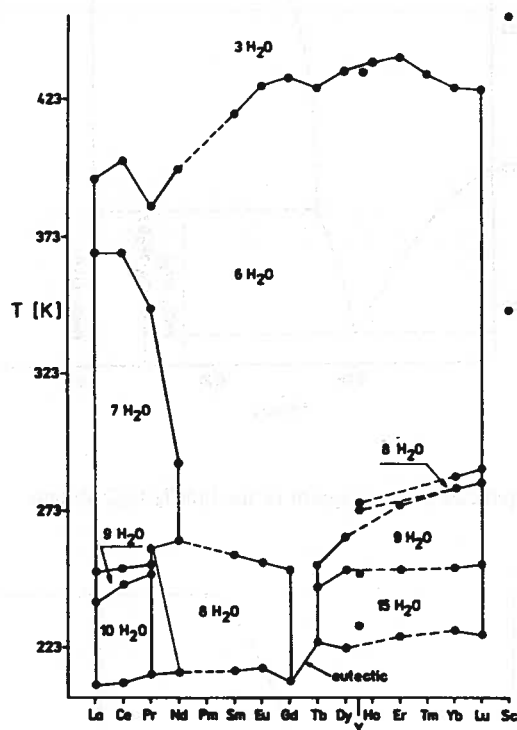


Fig. 4. Characteristic experimental temperatures of the binary phase diagrams of the $\text{LnCl}_3\text{-H}_2\text{O}$ systems

Interpolating the corresponding eutectic and peritectic points determined, one may presume an existence of the characteristic solid phases and their melting temperatures which were not determined in the experiments. On this basis, the unknown $\text{PmCl}_3\text{-H}_2\text{O}$, $\text{HoCl}_3\text{-H}_2\text{O}$ and $\text{TmCl}_3\text{-H}_2\text{O}$ phase diagrams were predicted. Such method is especially important in the case of the $\text{PmCl}_3\text{-H}_2\text{O}$ system because it is practically impossible to prepare PmCl_3 at concentration proper for thermal analysis due to the high radioactivity of Pm and significant self heating of the element and its compounds. The predicted $\text{PmCl}_3\text{-H}_2\text{O}$ phase diagram is shown in Fig. 5. An existence of $\text{PmCl}_3 \cdot 7\text{H}_2\text{O}$ (marked with the question mark) is only a supposition at temperatures lower than the peritectic decomposition of $\text{PmCl}_3 \cdot 8\text{H}_2\text{O}$ as it could be deduced from an extrapolation of the dependence of the peritectic temperatures for the $\text{RECl}_3 \cdot 7\text{H}_2\text{O}$ type of salts to the position of PmCl_3 ; see Fig. 4.

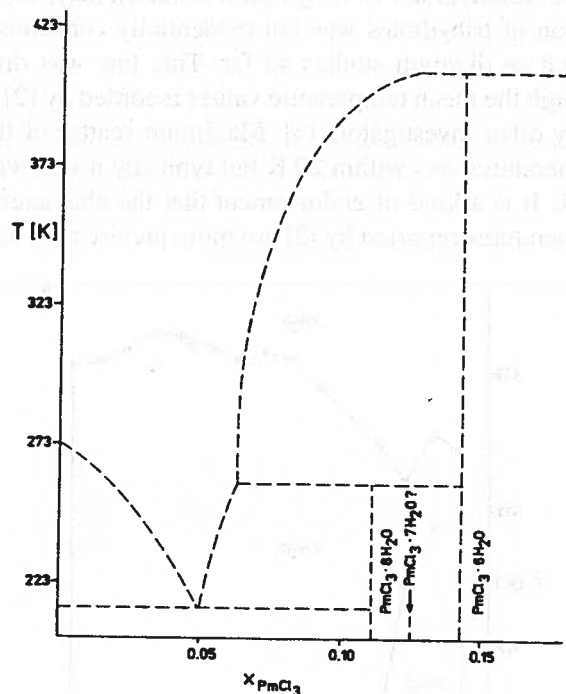


Fig. 5. Predicted phase diagram of the $\text{PmCl}_3\text{-H}_2\text{O}$ system

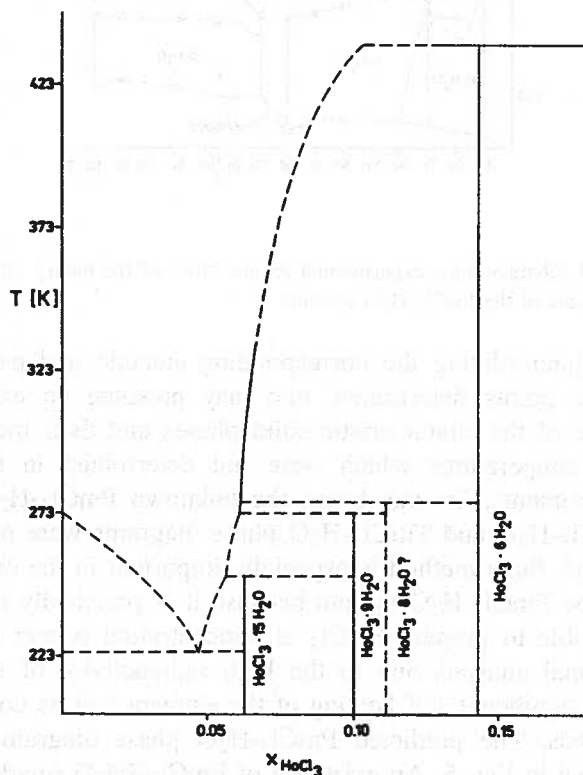


Fig. 6. Predicted phase diagram of the $\text{HoCl}_3\text{-H}_2\text{O}$ system

Phase diagrams for the $\text{HoCl}_3\text{-H}_2\text{O}$ and $\text{TmCl}_3\text{-H}_2\text{O}$ systems were predicted in the similar way. Only a part of the liquidus is known for HoCl_3 between 273 and 333 K

what is reflected by the continuous line showed in the partial phase diagram for the $\text{HoCl}_3\text{-H}_2\text{O}$ system, as depicted in Fig. 6. It was difficult to exclude a formation of $\text{HoCl}_3 \cdot 8\text{H}_2\text{O}$ because as it comes from the integrated form of the diagrams shown in Fig. 4, the octahydrates were found to be the equilibrium solids to the saturated solutions within the narrow ranges of few K in the case of YCl_3 , YbCl_3 and LuCl_3 , thus an octahydrate may be also present in the case of HoCl_3 and TmCl_3 . The predicted $\text{TmCl}_3\text{-H}_2\text{O}$ phase diagram looks analogically to the one shown in Fig. 6 for the $\text{HoCl}_3\text{-H}_2\text{O}$ system, differing only in the eutectic and peritectic temperatures which for the TmCl_3 may be read-out from the integrated diagram in Fig. 4.

It would be advisable in future to complement the thermal analyses of these systems with x-ray diffraction studies of the separated phases at low temperatures because except the systematic investigations of the isotypic trihydrates at elevated temperatures [8], hexahydrates and heptahydrates at room temperature [4] only $\text{YbCl}_3 \cdot 9\text{H}_2\text{O}$ was structurally studied at 263 K [9], so far.

4. Ternary systems

As it was mentioned in the introduction, the largest part of the evaluation [1] is devoted to the ternary systems. Predominantly, one ternary system was investigated in one paper, therefore there is not much material for a quantitative comparison. The $\text{LaCl}_3\text{-HCl-H}_2\text{O}$ system is the only example when the solubility values from several papers could be compared. The corresponding data at 298 K are shown in Fig. 7. Although the general dependence of the LaCl_3 solubility versus HCl concentration is qualitatively similar in 6 publications and the equilibrium solid phase was always identified as $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ at this and other temperatures (273–363 K), scatter of the experimental solubility results from various sources increased from only few % in water to about 15% at the highest HCl content. This confrontation of the data is not optimistic and suggests that a greater caution ought to be applied to the quantitative aspect of the solubility results in the ternary and quaternary systems than in the binary systems.

An important group of studies of the ternary systems $\text{RECl}_3\text{-MCl}_x\text{-H}_2\text{O}$ is related to those with alkali metal chlorides. Generally, light alkali metals (Li, Na, K) do not form ternary compounds with RECl_3 as Rb and Cs do. Stoichiometries of these ternary compounds (double salts) are frequently the same as those formed in the binary salt systems $\text{RECl}_3\text{-MCl}$, for example: Cs_3LaCl_6 [10] and $\text{Cs}_3\text{LaCl}_6 \cdot 3\text{H}_2\text{O}$ [11] or Cs_2EuCl_5 [10] and $\text{Cs}_2\text{EuCl}_5 \cdot 4\text{H}_2\text{O}$ [11], respectively. The hydrat-

ed salts obtained this way could be further dehydrated [11]. Therefore, the synthesis method in the aqueous medium at ambient temperature seems to be technologically more attractive and less-energy consuming than the synthesis of such compounds in the molten salt systems. A formation of an anhydrous equivalent to $\text{Cs}_5\text{EuCl}_8 \cdot 14\text{H}_2\text{O}$ [11] was not observed in the corresponding binary EuCl_3 - CsCl system.

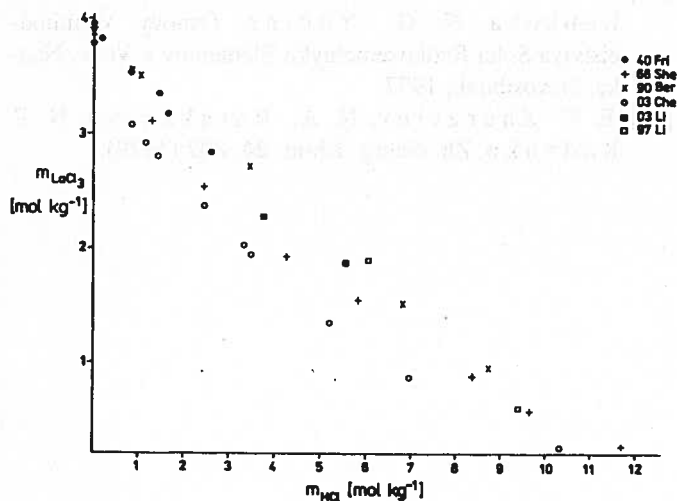


Fig. 7. The solubility of LaCl_3 in aqueous HCl solutions at 298 K

No formation of ternary compounds was observed in the case of alkaline earth metal chlorides and such ternary systems were found to be of eutonic type. However, various compounds were formed between RECl_3 and ZnCl_2 or CdCl_2 in the aqueous medium. For example, $\text{Cd}_5\text{Y}_2\text{Cl}_{16} \cdot 26\text{H}_2\text{O}$, $\text{Cd}_4\text{YCl}_{11} \cdot 13\text{H}_2\text{O}$ and $\text{Cd}_8\text{YCl}_{19} \cdot 15\text{H}_2\text{O}$ compounds were identified in the CdCl_2 - YCl_3 - H_2O system and they were characterized by different instrumental methods [12]. These compounds could be also dehydrated. No compounds were found in case of the CuCl_2 - LaCl_3 - H_2O system [1].

The ternary systems containing two rare earth chlorides in water were very intensively investigated by Nikolaev and coworkers [13]. If ionic radii of both rare earth metals were similar and the solid chloride hydrates belonged to the same type of crystal structure then they could form a continuous series of solid solutions as the equilibrium phase. The higher was the difference between the ionic radii the wider was a miscibility gap between them. In the systems containing one heptahydrate and one hexahydrate the solid immiscibility range was always observed.

Many solubility experiments were performed with ternary systems containing organic compounds. They may be divided in two groups: (i) with hydrochlorides of amines or aminoacids and (ii) with non-electrolyte molecules. Zhuravlev and coworkers [14] showed,

for example, that composition of the complex compounds identified in the aqueous RECl_3 systems with trimethylamine hydrochloride (teahc) (RECl_3 :teahc = 1:5, 1:4, 1:4, 1:4, 1:3, 1:3 and 1:4, for La, Ce, Pr, Nd, Sm, Gd and Dy, respectively) changed in the lanthanide series and did not show any regularity. However, in the case of urea a certain regularity in stoichiometry of the compounds determined was observed what is shown in Table 3. All rare earth metal chlorides form anhydrous complexes with 6 molecules of urea, majority of them forms ones with 4 molecules of urea and only few rare earth metal chlorides form complexes of untypical stoichiometry.

TABLE 3

Complex salt formation (denoted with - X) between rare earth metal chlorides and urea ($\text{CH}_4\text{N}_2\text{O}$) according to the literature data collected in [1]

Element	$\text{RECl}_3 \cdot 6\text{CH}_4\text{N}_2\text{O}$	$\text{RECl}_3 \cdot 4\text{CH}_4\text{N}_2\text{O}$	Other compounds formed
La	X	-	$\text{LaCl}_3 \cdot \text{CH}_4\text{N}_2\text{O}$
Ce	X	X	-
Pr	X	X	-
Nd	X	X	-
Sm	X	X	-
Gd	X	X	-
Dy	X	X	-
Ho	X	X	-
Er	X	X	$\text{ErCl}_3 \cdot 2\text{CH}_4\text{N}_2\text{O} \cdot 6\text{H}_2\text{O}$
Tm	X	-	$\text{TmCl}_3 \cdot 2\text{CH}_4\text{N}_2\text{O} \cdot 4\text{H}_2\text{O}$
Yb	X	-	$\text{YbCl}_3 \cdot \text{CH}_4\text{N}_2\text{O}$
Y	X	X	$2\text{YCl}_3 \cdot 3\text{CH}_4\text{N}_2\text{O} \cdot 4\text{H}_2\text{O}$

5. Quarternary systems

The individual studies of some quarternary systems do not allow for any generalizations. The only exception are the experiments concerned with three RECl_3 salts present simultaneously in water [13] where a formation of the corresponding solid solution was observed when ionic radii of the RE metals were very similar, as it was observed by analogy for the ternary systems.

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Compound	Crystal Structure	Space Group	Cell Parameters (Å)	Z
LiClO ₄	Orthorhombic	Cmca	a = 10.10, b = 4.20, c = 4.20	4
LiClO ₃	Trigonal	R-3m	a = 4.20, c = 10.10	2
LiClO ₂	Trigonal	R-3m	a = 4.20, c = 10.10	2
LiClO	Trigonal	R-3m	a = 4.20, c = 10.10	2
LiCl	Trigonal	R-3m	a = 4.20, c = 10.10	2
LiClO ₄ ·H ₂ O	Orthorhombic	Cmca	a = 10.10, b = 4.20, c = 4.20	4
LiClO ₃ ·H ₂ O	Trigonal	R-3m	a = 4.20, c = 10.10	2
LiClO ₂ ·H ₂ O	Trigonal	R-3m	a = 4.20, c = 10.10	2
LiClO·H ₂ O	Trigonal	R-3m	a = 4.20, c = 10.10	2
LiCl·H ₂ O	Trigonal	R-3m	a = 4.20, c = 10.10	2

The structural analysis of compounds was carried out on the diffractometer "Diffractometer" (CuKα radiation, λ = 1.5418 Å) with graphite monochromator. The only absorption correction was applied with the use of the program "CORRECT" in the "SHELX" package. The structure was solved by direct methods and refined by full-matrix least-squares method on F². The R and wR indices were 0.032 and 0.080, respectively. The data were collected on a Siemens diffractometer with graphite monochromator. The structure was solved by direct methods and refined by full-matrix least-squares method on F². The R and wR indices were 0.032 and 0.080, respectively.

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The formation of lithium perchlorate was observed in the case of solution of lithium chloride and lithium nitrate salts. In the case of solution of lithium chloride and lithium nitrate salts, the formation of lithium perchlorate was observed in the case of solution of lithium chloride and lithium nitrate salts. The formation of lithium perchlorate was observed in the case of solution of lithium chloride and lithium nitrate salts. The formation of lithium perchlorate was observed in the case of solution of lithium chloride and lithium nitrate salts.

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Many similar experiments were performed with various salts containing lithium perchlorate. The results are given in Table 1. It is seen from the data that the formation of lithium perchlorate is observed in the case of solution of lithium chloride and lithium nitrate salts. The formation of lithium perchlorate was observed in the case of solution of lithium chloride and lithium nitrate salts.