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Phase equilibria in the $Mg(NO_3)_2$–$Ln(NO_3)_3$ (Ln = La, Ce, Pr)–HNO_3 (~21%)–H_2O systems at 298.15 K and thermodynamic properties of $3Mg(NO_3)_2 \cdot 2Ln(NO_3)_3 \cdot 24H_2O$

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ABSTRACT

The solid-liquid equilibria of the $Mg(NO_3)_2$–$Ln(NO_3)_3$ (Ln = La, Ce, Pr)–HNO_3–H_2O systems in the (~21%) HNO_3 regions at $T = 298.15$ K were studied by using the method of isothermal solubility, the phase diagrams were obtained based on the measured data. The Schreinemaker's wet residues method was used to determine the compositions of solid-phases. The three quaternary systems are all composed of three equilibrium solid-phases $Mg(NO_3)_2 \cdot 6H_2O$, $3Mg(NO_3)_2 \cdot 2Ln(NO_3)_3 \cdot 24H_2O$, $Ln(NO_3)_3 \cdot 6H_2O$. The new solid-phase compounds $3Mg(NO_3)_2 \cdot 2La(NO_3)_3 \cdot 24H_2O$, $3Mg(NO_3)_2 \cdot 2Ce(NO_3)_3 \cdot 24H_2O$ and $3Mg(NO_3)_2 \cdot 2Pr(NO_3)_3 \cdot 24H_2O$ are congruently soluble in an average medium of ~21 mass% HNO_3, and they were characterized by chemical analysis, X-ray diffraction (XRD), X-ray diffraction single crystal structure analysis, and thermogravimetric/differential thermogravimetric (TG–DTG) techniques. The XRD graphs of $3Mg(NO_3)_2 \cdot 2La(NO_3)_3 \cdot 24H_2O$, $3Mg(NO_3)_2 \cdot 2Ce(NO_3)_3 \cdot 24H_2O$ and $3Mg(NO_3)_2 \cdot 2Pr(NO_3)_3 \cdot 24H_2O$ are identical due to their isomorphic structure. The X-ray diffraction single crystal structure analysis show that $3Mg(NO_3)_2 \cdot 2Ln(NO_3)_3 \cdot 24H_2O$ (Ln = La, Ce, Pr) all belong to hexagonal systems, with space group R_3, for $3Mg(NO_3)_2 \cdot 2La(NO_3)_3 \cdot 24H_2O$, $a = b = 1.1082 \pm 0.0009$ nm, $c = 1.7422 \pm 0.0013$ nm, $V = 1.853 \pm 0.002$ nm^3, $D_c = 3.976$ g·cm^{-3}, $Z = 3$, for $3Mg(NO_3)_2 \cdot 2Ce(NO_3)_3 \cdot 24H_2O$, $a = b = 1.1056 \pm 0.0003$ nm, $c = 1.7438 \pm 0.0009$ nm, $V = 1.8462 \pm 0.0008$ nm^3, $D_c = 3.997$ g·cm^{-3}, $Z = 3$, for $3Mg(NO_3)_2 \cdot 2Pr(NO_3)_3 \cdot 24H_2O$, $a = b = 1.0992 \pm 0.0009$ nm, $c = 1.7211 \pm 0.0007$ nm, $V = 1.8012 \pm 0.0013$ nm^3, $D_c = 4.101$ g·cm^{-3}, $Z = 3$. The $\Delta_{sol}H_m^0$ (standard molar enthalpies of solution) of the compounds $3Mg(NO_3)_2 \cdot 2La(NO_3)_3 \cdot 24H_2O$, $3Mg(NO_3)_2 \cdot 2Ce(NO_3)_3 \cdot 24H_2O$ and $3Mg(NO_3)_2 \cdot 2Pr(NO_3)_3 \cdot 24H_2O$ in water (aq) were measured to be (107.96 ± 0.74) kJ·mol^{-1}, (110.18 ± 0.54) kJ·mol^{-1} and (102.96 ± 0.55) kJ·mol^{-1}, respectively, and their $\Delta_f H_m^0$ (standard molar enthalpies of formation) were calculated to be $-(12242.6 \pm 2.5)$ kJ·mol^{-1}, $-(12223.1 \pm 2.4)$ kJ·mol^{-1} and $-(12232.6 \pm 2.5)$ kJ·mol^{-1}, respectively.

1. Introduction

It has been found that compounds with lanthanide ions exhibit extraordinary physical and biological function, some of them have been applied in many fields [1–8]. In industry, they are used: for glasses, phosphors, magnetism and lasers. A lot of applications are found in biology: as luminescent probes in the investigation of binding sites in proteins, labels in immunoassays and in noninvasive tests, improve growth and development of plants at a suitable concentration. Moreover, magnesium oxide/rare earth oxide composites exhibited a good performance as catalysis in oxidative coupling of methane and dimethyl carbonate synthesis [9,10]. The thermodynamic properties of compounds are important in science studies and practical applications, researchers are pay close attention to the work of searching, finding and characterizing the basic thermodynamic properties of new compounds containing lanthanides.

In order to separate the rare-earth element by phase equilibrium method, the ternary systems $CeCl_3$–$MgCl_2$–H_2O and $Mg(NO_3)_2$–$Ln(NO_3)_3$–H_2O (Ln = La, Ce, Pr, Nd, Sm, Gd, Dy, Y) were studied and evaluated [11,12]. The system $CeCl_3$–$MgCl_2$–H_2O was simple eutonic type. In the systems $Mg(NO_3)_2$–$Ln(NO_3)_3$–H_2O (Ln = La, Ce, Pr, Nd, Sm), the new solid-phase compounds $3Mg(NO_3)_2 \cdot 2Ln(NO_3)_3 \cdot 24H_2O$ were formed, while the $Mg(NO_3)_2$–$Ln(NO_3)_3$–H_2O (Ln = Gd, Dy, Y) systems were found to be simple systems. The literature [12] only provides double saturation point data and phase diagram, but not involve the characterization of

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the new solid-phase compounds. In addition, Bunyakina et al. [13]. re-examined the ternary system $Mg(NO_3)_2$–$Nd(NO_3)_3$–H_2O and confirmed that the phase chemical relation was consistent with that of Ref. [12]. However, the compound $3Mg(NO_3)_2{\cdot}2Nd(NO_3)_3{\cdot}24H_2O$ was also not characterized.

In the salt-water systems, it may change the phase chemical relation when the added acid reaches a certain amount [14]. To investigate the phase equilibria of the quaternary systems $Mg(NO_3)_2$–$Ln(NO_3)_3$–HNO_3–H_2O, compare phase relationship with the ternary systems $Mg(NO_3)_2$–$Ln(NO_3)_3$–H_2O, and provide the phase diagrams at T = 298.15 K for researchers. The present paper reports the solubility and phase equilibrium relations of the $Mg(NO_3)_2$–$Ln(NO_3)_3$ (Ln = La, Ce, Pr)–HNO_3 (~21%)–H_2O systems at T = 298.15 K and the thermodynamic properties of three new solid-phase compounds established in the systems.

2. Experimental

2.1. reagents

All reagents and solvents employed were commercially available and used without further purification. Double deionized water was used (resistivity = 5.7 MΩ·cm). Table 1 summarizes relevant information on sample material purity.

2.2. Investigations on the systems at T = 298.15 K and analysis methods

The solubility of the $Mg(NO_3)_2$–$Ln(NO_3)_3$ (Ln = La, Ce, Pr)–HNO_3 (~21%)–H_2O systems were investigated according to Ref. [15]. Different samples were first assigned on the phase diagram cross-section on which the HNO_3 mass percentage of the liquid phase is 21 mass%. Different mass ratios of $Mg(NO_3)_2{\cdot}6H_2O$, $Ln(NO_3)_3{\cdot}6H_2O$, H_2O, and 65 mass% nitric acid were mixed for each sample according to the mass percentage of the different points of the quaternary systems $Mg(NO_3)_2$–$Ln(NO_3)_3$ (Ln = La, Ce, Pr)–HNO_3–H_2O projected on the trigonal basal face $Mg(NO_3)_2$–$Ln(NO_3)_3$ (Ln = La, Ce, Pr)–H_2O. Each sample containing solid and liquid phases was sealed in a plastic container. The acidity of the liquid phase of every sample was kept at 21 mass% HNO_3. All the sealed samples were put in the constant temperature water tank. The temperature was fixed at 298.15 K. The accuracy of the temperature was 0.1 K. The acidity (HNO_3 mass%) of the liquid phase could deviate from 21 mass% on the first 1–2 days due to the gradual establishment of equilibrium in the systems. As a consequence, the liquid phase of the samples may vary from 21 mass% HNO_3 and was subsequently adjusted to this concentration. This process was done repetitively until the HNO_3 mass percentage in liquid phase was maintained at about 21 mass%. The samples were sealed again and agitated continuously for another 1–2 days until a new equilibrium was attained. The composition of the saturated solutions and the corresponding solid (wet residue point) was established after the composition no longer changed. As we all know, in the equilibrium liquid phases, the concentration of HNO_3 was very difficult to hold a constant value on the cross section. So we only could get an average value via the experiment. In the present work we only gave cross section results of the $Mg(NO_3)_2$–$Ln(NO_3)_3$–HNO_3–H_2O quaternary systems at an average concentration of ~21 mass% HNO_3.

After the systems reached equilibrium, the liquid phases, after weighing accurately, added into a 100 mL volumetric flask and diluted with deionised water. The wet residues were removed into a weighing bottle by a scoop. Similarly, the weight of wet residues was measured. Afterwards these were dissolved by deionised water, transferred the solution to a 100 mL volumetric flask, and diluted with deionised water. The weighing bottle was rinsed 4–5 times to ensure that all wet residues were transferred into flask. Finally, these samples were analyzed quantitatively.

The analysis methods were as follows: (1) the content of H^+ was analyzed by titration with a solution of sodium hydroxide; (2) the content of Ln^{3+} was determined by titration with EDTA solution in the presence of buffer (pH ~ 5.5); (3) the content of Mg^{2+} was determined by titration with EDTA solution in the presence of buffer (pH ~ 10.0).

The solid phases formed in the studied systems were determined by Schreinemakers' method of wet residues [16].

Table 1
Reagents used in this study.

Reagent	Source	State	Mass fraction purity
$Mg(NO_3)_2{\cdot}6H_2O$	Sinopharm Chemical Reagent Co., Ltd.	Solid	0.995[a]
$La(NO_3)_3{\cdot}6H_2O$	Shanghai Aladdin biochemical technology Co., Ltd.	Solid	0.999[a]
$Ce(NO_3)_3{\cdot}6H_2O$	Shanghai Aladdin biochemical technology Co., Ltd	Solid	0.999[a]
$Pr(NO_3)_3{\cdot}6H_2O$	Shanghai Aladdin biochemical technology Co., Ltd	Solid	0.999[a]
Nitric acid	Luoyang Haohua Chemical Reagent Company	Aqueous	Guaranteed reagent [a]
$3Mg(NO_3)_2{\cdot}2La(NO_3)_3{\cdot}24H_2O$	Synthesized	Solid	0.994[b]
$3Mg(NO_3)_2{\cdot}2Ce(NO_3)_3{\cdot}24H_2O$	Synthesized	Solid	0.993[b]
$3Mg(NO_3)_2{\cdot}2Pr(NO_3)_3{\cdot}24H_2O$	Synthesized	Solid	0.994[b]

[a] As stated by the supplier.
[b] Evaluated by averaging based on the measured contents of $Mg(NO_3)_2$, $La(NO_3)_3$, $Ce(NO_3)_3$ and $Pr(NO_3)_3$.

2.3. Synthesis of 3Mg(NO3)2·2Ln(NO3)3·24H2O (Ln = La, Ce, Pr)

Based on the phase regions where $3Mg(NO_3)_2{\cdot}2Ln(NO_3)_3{\cdot}24H_2O$ (Ln = La, Ce, Pr) are in $Mg(NO_3)_2$–$Ln(NO_3)_3$–HNO_3 (~21%)–H_2O systems, $Mg(NO_3)_2$, $Ln(NO_3)_3$, HNO_3 and H_2O were mixed and agitated at T = 298.15 K under the condition of the mole ratio of water and nitrate was 3:2 and concentration of HNO_3 about 21 mass%. Upon the (solid + liquid) equilibrium was attained, the solid $3Mg(NO_3)_2{\cdot}2Ln(NO_3)_3{\cdot}24H_2O$ were collected by suction filtration method.

2.4. Equipments and conditions

TG–DTG analysis was undertaken with a NETZSCH STA449C thermal analysis apparatus with a heating rate of 10 $K{\cdot}min^{-1}$ under a N_2 atmosphere with a flow rate of 100 $cm^3{\cdot}min^{-1}$. XRD measurements were performed by a D/Max–3C diffractometer using Cu Kα radiation at T = 298.15 K, $u(T)$ = 1.0 K. The diffraction data of the structure analysis were collected by a Bruker Smart Apex–II CCD diffractometer using graphite monochromatized Mo Kα radiation (λ = 0.071073 nm), at T = 298.15 K, $u(T)$ = 1.0 K.

2.5. Calorimetric technique

The enthalpies of solution were measured with RD496-2000 heat conduction microcalorimeter (Mianyang CP Thermal Analysis Instrument Co., LTD, China) [17]. The enthalpy of solution of KCl (mass fraction ⩾0.9999) in deionized water was measured to verify the reliability of the calorimeter. The mean value (17.59 ± 0.10)