Phase Equilibrium of the $La(NO_3)_3$—Phe—H_2O System at 298.15 K and the Preparation and Characterization of Complexes

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The solubility properties of the $La(NO_3)_3$—Phe—H_2O (Phe = D,L-β-phenyl-α-alanine) system at 298.15 K in the whole concentration range have been investigated by the semimicrophase equilibrium method. The corresponding solubility diagram and refractive index diagram were constructed. The results indicated that there were two stoichiometric complexes formed in this system, namely: $La(Phe)(NO_3)_3 \cdot 5H_2O$ and $La(Phe)_2(NO_3)_3 \cdot 3H_2O$. Both the complexes are incongruently soluble in water. Based on phase equilibrium data, two kinds of complexes were prepared. Their composition and properties were investigated by chemical amalysis, elemental analysis, IR spectra, and DTG-TG.

Lanthanide ions possess some special functions in biological body and they are often used as promoters in the textile dyeing industry, and diagnostic agents in clinical medicine [1—6]. Amino acids are the basic units of proteins. It has become more important to understand the behaviour of lanthanide ions in biological systems. Therefore, studies of the lanthanide complexes with amino acids are of interest. The investigation on the interaction between lanthanide salts and amino acids in the whole concentration range by the phase equilibrium method can provide a thermodynamic basis of the preparation of complexes, and avoid blindness in the synthesis process. Study on coordination behaviour between rare earth nitrate and phenylalanine has not yet been reported in the literature.

In this work, the solubility properties of the $La(NO_3)_3$—Phe—H_2O system at 298.15 K in the whole concentration range have been investigated by the semimicrophase equilibrium method [7].

EXPERIMENTAL

$La(NO_3)_3 \cdot 6H_2O$ was prepared according to Ref. [8] and its composition and purity were determined by EDTA titration and by measuring of the melting point. D,L-β-Phenyl-α-alanine (Phe) was of a biochemical (chromatographic purity) and others of analytical purity.

Thermostat, the temperature fluctuation $\pm$ 0.05 K, was made by ourselves. WZS-1 type Abbe refractometer, ZD-2 type automatical potential titrator, IR-440 model infrared spectrophotometer, and PE-TGS-7 thermogravimetric analyzer were used. The ther-mometer, weights, and all measuring vessels were calibrated.

The content of La^{3+} was determined complexometrically with EDTA. Phe was determined by the formalin method [9]. Before it was titrated, the La^{3+} was screened by precipitating with $K_2C_2O_4$. Water content was determined by the volatilization-mass loss method. Analytical results of the known samples, which were exactly prepared from $La(NO_3)_3 \cdot 6H_2O$, Phe, and H_2O (Table 1) indicated that analytical errors were $\leq$ 0.2 % .

Based on phase equilibrium data the points were selected in the two-phase regions, corresponding to complexes *I* and *II*, then the samples were prepared, sealed in polyvinyl tubes, fixed in turntable and turned until equilibrium. In order to achieve the highest possible removal of mother solution from wet residue, samples were separated by centrifuging, washed with ethanol and dried in different drying conditions until their mass became constant.

RESULTS AND DISCUSSION

There are two phase equilibrium methods commonly used in thermodynamics, namely "Schreimaker's wet residue" and "synthetic complex" method. Consumption of system components is (20—30) g. Therefore, these two methods are hardly to be used in thermodynamic systems concerning rare precious substances and organic solvent. In order to improve these two methods, *Jiang et al.* [7] have designed a semimicro method for studying phase equilibrium, in which "wet residue" method and "synthetic complex" method were simultaneously applied. Consumption of

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Table 1. Analytical Results of Samples

Complex	w_i(calc.)/% w_i(found)/%		
	$La(NO_3)_3$	Phe	H_2O
I	57.75	29.40	12.85
	57.69	29.44	12.87
II	53.67	33.33	13.00
	53.68	33.36	12.96

system components is only one tenth of the above-mentioned macro method or even less.

The samples being used in the studied system were exactly prepared and sealed in the polyvinyl tubes. These tubes were fixed on the turntable and turned until equilibrium. We have investigated the ternary system $La(NO_3)_3$—Phe—H_2O at 298.15 K by the above-mentioned semimicro method. The results showed that the equilibrium of this system was reached after stirring in the thermostat for 40 d.

The solubility and refractive index data of the system $La(NO_3)_3$—Phe—H_2O at 298.15 K are presented in Table 2. Figs. 1 and 2 show the solubility diagram and refractive index curve of saturated solutions of
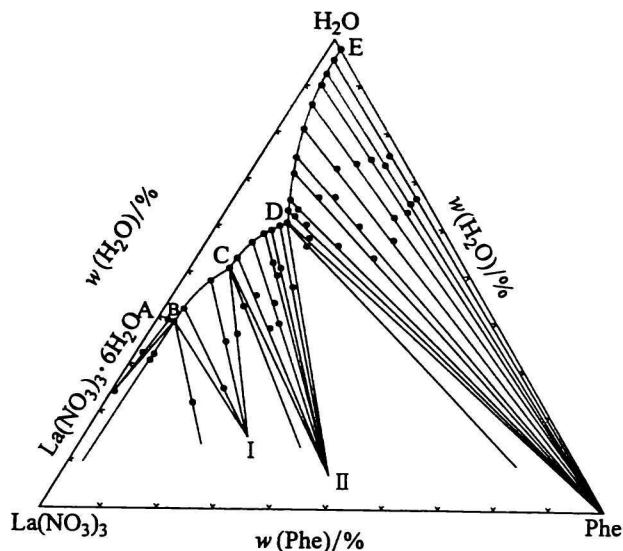
Fig. 1. Solubility diagram of the ternary system $La(NO_3)_3$—Phe—H_2O at 298.15 K.

the ternary system $La(NO_3)_3$—Phe—H_2O at 298.15 K, respectively.

As shown in Figs. 1 and 2, the solubility curve and refractive index curve of saturated solutions of

Table 2. Solubility and Refractive Index Data of the System $La(NO_3)_3$—Phe—H_2O at 298.15 K

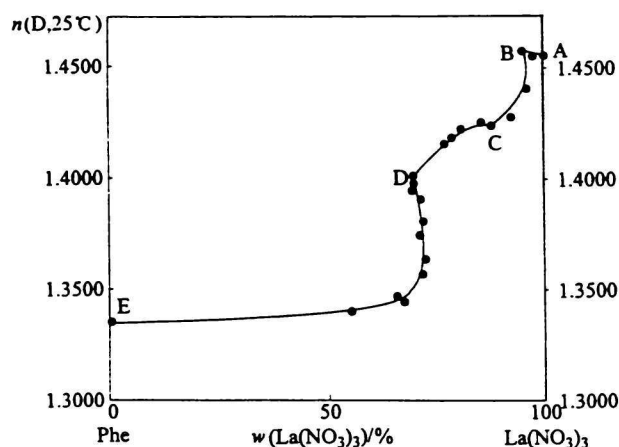| w_i(Complex)/%		w_i(Solutions)/%		w_i(Residues)/%		Equilibrium solid phase	$w_i(La(NO_3)_3) \times 100$ $w_i(La(NO_3)_3) + w_i(Phe)$	Refractive index n_D(25 °C)
$La(NO_3)_3$	H_2O	$La(NO_3)_3$	H_2O	$La(NO_3)_3$	H_2O			
—	—	59.89	40.11	—	—	$La(NO_3)_3 \cdot 6H_2O$	100.00	1.4590
66.36	32.43	58.10	39.83	68.75	29.96	$La(NO_3)_3 \cdot 6H_2O$	99.56	1.4600
—	—	57.25	39.55	62.68	22.35	$I+ La(NO_3)_3 \cdot 6H_2O$	94.71	1.4607
64.92	32.12	57.32	39.49	65.18	31.59	$I+ La(NO_3)_3 \cdot 6H_2O$	94.73	1.4609
—	—	54.36	43.13	55.09	25.93	I	95.59	1.4435
50.32	35.27	46.63	48.99	—	—	I	91.41	1.4306
—	—	42.51	50.92	47.05	39.03	I	86.61	1.4259
—	—	42.43	50.97	43.60	44.17	$I + II$	86.54	1.4255
40.14	45.76	39.32	53.68	41.14	38.01	II	84.89	1.4260
37.28	46.48	35.44	56.31	37.63	44.20	II	81.12	—
—	—	35.00	56.55	39.05	39.70	II	80.55	1.4251
33.89	52.10	32.67	58.32	34.62	49.93	II	78.38	1.4208
—	—	31.50	58.95	35.49	45.84	II	76.74	—
—	—	31.13	59.04	33.33	51.33	II	76.00	1.4179
—	—	28.23	60.67	33.05	47.01	II	71.78	—
—	—	27.51	60.78	25.79	·56.70	Phe + II	70.14	1.4025
25.21	57.84	27.09	61.22	18.00	42.25	Phe	69.86	1.4000
25.10	62.90	25.36	63.42	24.29	60.37	Phe	69.33	1.3960
24.31	63.99	24.53	65.29	20.41	56.21	Phe	70.67	1.3922
18.90	66.72	20.83	70.76	15.45	53.90	Phe	71.24	1.3815
16.00	66.54	18.28	73.99	14.36	60.68	Phe	70.28	1.3745
12.56	72.92	14.22	80.26	10.05	57.35	Phe	72.04	1.3645
8.95	73.23	10.33	85.30	7.61	62.47	Phe	70.27	1.3564
5.91	74.45	6.60	89.95	4.77	63.63	Phe	65.67	1.3489
4.04	73.80	4.96	92.52	3.53	65.55	Phe	66.31	1.3451
2.01	75.43	2.50	95.48	1.81	66.80	Phe	54.70	1.3410
—	—	—	98.05	—	—	Phe	0.00	1.3358

Fig. 2. Refractive index curve of saturated solutions of the ternary system La(NO$_3$)$_3$—Phe—H$_2$O at 298.15 K.

Fig. 3. Comparison of solubility diagrams of the RE(NO$_3$)$_3$—Phe—H$_2$O (RE = La, Yb) systems at 298.15 K. ——— La(NO$_3$)$_3$, - - - Yb(NO$_3$)$_3$.

· 3H$_2$O, and phenylalanine, respectively; B is eutonic point to La(NO$_3$)$_3$ · 6H$_2$O with complex I; C is the complex I with complex II; D is the complex II with Phe. This system is invariant at B, C, D, E points in the solubility diagram of the given system, there are no degrees of freedom, F = 0, by the phase rule, therefore, these points are also invariant points; the phase region of La(NO$_3$)$_3$ · 6H$_2$O is quite small, therefore the curve AB is very short; there are two stoichiometric complexes formed in this system, their compositions are given in Table 3. Both complexes are incongruently soluble in water. This may be an important reason why the solid complexes of rare earth nitrate with phenylalanine have not yet been reported in the literature for a long time.

The influence of lanthanide ions on complex formation has been studied. Comparing the La(NO$_3$)$_3$—Phe—H$_2$O system at 298.15 K with the Yb(NO$_3$)$_3$—Phe—H$_2$O system at 298.15 K (Fig. 3) it is found that there are three kinds of complexes formed in the Yb(NO$_3$)$_3$—Phe—H$_2$O system, while only two kinds of complexes, namely: La(Phe)(NO$_3$)$_3$ · 5H$_2$O and La(Phe)$_2$(NO$_3$)$_3$ · 3H$_2$O are formed in the studied system. The difference of cations of RE(NO$_3$)$_3$ does affect the kind of complexes formed in these systems, as well as the size of the phase regions of RE(Phe)(NO$_3$)$_3$ · nH$_2$O and RE(Phe)$_2$(NO$_3$)$_3$ · nH$_2$O. The phase regions of RE(Phe)(NO$_3$)$_3$ · nH$_2$O become larger when going from La to Yb, while the phase regions of RE(Phe)$_2$(NO$_3$)$_3$ · nH$_2$O become smaller.

Individual amino acids influenced the complex formation. Comparisons of some properties of amino acids (Am, R—CH(NH$_2$)—COOH: phenylalanine (Phe), glycine (Gly), glutamine (Glu)) and main results of the La(NO$_3$)$_3$—Am—H$_2$O systems [10, 11] are given in Table 4.

The difference of amino acids does affect the kind and properties of complexes formed in these systems. The complexes formed in the studied system are incongruently soluble in water, while both complexes formed in the La(NO$_3$)$_3$—Gly—H$_2$O system are congruently soluble in water.

The analytical results of composition of the obtained complexes at different drying conditions are given in Table 5.

The following conclusions can be drawn from IR spectra of complexes III, IV, and Phe: There exists a characteristic absorption of —NH$_3^+$ and

the system La(NO$_3$)$_3$—Phe—H$_2$O at 298.15 K were exactly correspondent. The solubility curve ABCDE of this system is made of four portions, corresponding to the solid phases: La(NO$_3$)$_3$ · 6H$_2$O, complex I—La(Phe)(NO$_3$)$_3$ · 5H$_2$O, complex II—La(Phe)$_2$(NO$_3$)$_3$

Table 3. Chemical Composition and Mole Ratio of Components

Complex	w_i(in solubility diagram)/%			Mole ratio of components				
	La(NO$_3$)$_3$	Phe	H$_2$O	La(NO$_3$)$_3$	:	Phe	:	H$_2$O
I	56.00	28.47	15.53	1		1		5
II	45.81	46.57	7.62	1		2		3

Table 4. Properties of Amino Acids and Characterization of the $La(NO_3)_3$—Am—H_2O System
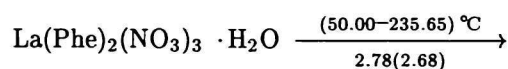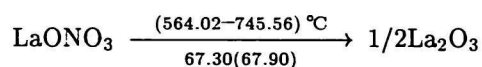
Acid	R	Properties	Isoelectric point	Solubility (25 °C, 100 g H_2O)/g	$n(La) : n(Am)$	Melting
Phe	$C_6H_5CH_2$	Nonpolarity	5.48	1.99	1 : 1	Incongruently
					1 : 2	Incongruently
Gly	H	Nonpolarity	5.97	24.99	1 : 2	Congruently
					1 : 4	Congruently
Glu	$HO_2C(CH_2)_2$	Acidity	3.22	0.84	—	—

Table 5. Composition of the Obtained Complexes

Complex	Drying condition	$w_i/\%$					Formula
		$La(NO_3)_3$	Phe	C	H	N	
I	Conc. H_2SO_4	63.85 (63.94)	31.56 (31.51)	21.36 (21.27)	2.65 (2.58)	11.18 (11.07)	$La(Phe)(NO_3)_3 \cdot H_2O$ (*III*)
II	Conc. H_2SO_4	48.31 (48.26)	49.12 (49.07)	32.34 (32.11)	3.52 (3.59)	10.58 (10.40)	$La(Phe)_2(NO_3)_3 \cdot H_2O$ (*IV*)
I	60 % H_2SO_4	59.60 (59.71)	30.41 (30.36)	19.93 (19.86)	3.23 (3.15)	10.41 (10.34)	$La(Phe)(NO_3)_3 \cdot 3H_2O$ (*V*)
II	60 % H_2SO_4	45.85 (45.81)	46.61 (46.57)	30.65 (30.48)	3.91 (3.98)	10.05 (9.92)	$La(Phe)_2(NO_3)_3 \cdot 3H_2O$ (*VI*)

—COO^- for complexes revealing that phenylalanine still keeps its zwitterion structure. Various vibrations of —NH_3^+ in complexes *III* and *IV* did not shift compared with those of free ligand. These results indicate that the N atom of NH_3^+ is not a coordinating one. ν_{as} (—COO^-) and ν_s(—COO^-) of complex *III* are shifted to higher frequencies compared with those of free ligand by 29 cm^{-1} and 22 cm^{-1}, respectively; similarly, ν_{as}(—COO^-) and ν_s(—COO^-) of complex *IV* are shifted by 35 cm^{-1} and 38 cm^{-1}, respectively. These results indicate that phenylalanine coordinates La^{3+} through O atoms of carboxyl group in these complexes. Broad bands appearing at 3350 cm^{-1} provide an evidence for the existence of H_2O molecules in these complexes.

Thermogravimetric analysis has been performed of two complexes. The thermal decomposition mechanism of these complexes may be determined according to TG curves as follows: Comparison of the found mass fraction loss/% with the calculated one was done.

$$La(Phe)(NO_3)_3 \cdot H_2O \xrightarrow[3.89(3.55)]{(50.00-340.05)\ °C}$$

$$La(Phe)(NO_3)_3 \xrightarrow[57.18(57.31)]{(340.05-564.02)\ °C}$$

$$LaONO_3 \xrightarrow[67.30(67.90)]{(564.02-745.56)\ °C} 1/2La_2O_3$$

$$La(Phe)_2(NO_3)_3 \cdot H_2O \xrightarrow[2.78(2.68)]{(50.00-235.65)\ °C}$$

$$La(Phe)_2(NO_3)_3 \xrightarrow[52.48(52.74)]{(235.65-533.39)\ °C}$$

$$La(NO_3)_3 \xrightarrow[73.80(75.81)]{(533.39-742.28)\ °C} 1/2La_2O_3$$
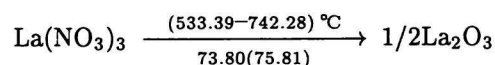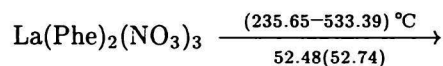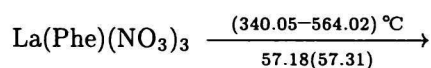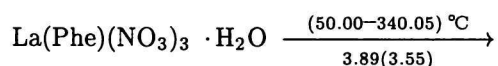
In order to examine the decomposition mechanism mentioned above, we have identified the intermediates during the thermal decompositions of complexes by IR spectra. As can be seen from equations, our suggestion of decomposition mechanism of complexes conforms to reality.

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