

Phase Chemistry of the $\text{YbCl}_3 \cdot 3\text{H}_2\text{O}$ — $18\text{C}6$ — $\text{C}_2\text{H}_5\text{OH}$ System at 298.15 K and Synthesis and Properties of Complexes

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The solubility properties of the $\text{YbCl}_3 \cdot 3\text{H}_2\text{O}$ — $18\text{C}6$ — $\text{C}_2\text{H}_5\text{OH}$ 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 three stoichiometric complexes formed in this system, namely: $3\text{YbCl}_3 \cdot 18\text{C}6 \cdot 9\text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH}$, $2\text{YbCl}_3 \cdot 18\text{C}6 \cdot 6\text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH}$, and $\text{YbCl}_3 \cdot 18\text{C}6 \cdot 3\text{H}_2\text{O}$. Both the former complexes are incongruently soluble in $\text{C}_2\text{H}_5\text{OH}$, while the third complex is congruently soluble in $\text{C}_2\text{H}_5\text{OH}$. The influence of lanthanide ions, anions, and solvent on formation of complexes has been examined and discussed. Based on phase equilibrium data, three kinds of complexes were prepared. Their composition and properties were investigated by chemical analysis, elemental analysis, IR spectra, DTG-TG and DSC.

Crown ethers and related macrocyclic and macropolycyclic molecules show a high complexation selectivity which makes them adequate ligands for the investigation of the coordinative properties of lanthanoid ions. The investigation on the interaction between lanthanoid salts and crown ethers in the whole concentration range by phase equilibrium method can provide the thermodynamic basis of the preparation of complexes, and avoid blindness in the synthesis preparation. As a part of a systematic investigation on the phase chemistry of the $\text{RECl}_3 \cdot 3\text{H}_2\text{O}$ — $18\text{C}6$ — $\text{C}_2\text{H}_5\text{OH}$ systems (RE = La, Pr, Gd) [1–3], this communication reports the studies on phase chemistry of the $\text{YbCl}_3 \cdot 3\text{H}_2\text{O}$ — $18\text{C}6$ — $\text{C}_2\text{H}_5\text{OH}$ system at 298.15 K and synthesis and properties of complexes.

EXPERIMENTAL

$\text{YbCl}_3 \cdot 3\text{H}_2\text{O}$ was prepared according to Ref. [4] and its composition and purity were determined by EDTA titration, and the Volhard method for the determination of chloride. Crown ether $18\text{C}6$ was of anal. grade purity, and it was dried over phosphoric oxide in a desiccator to constant mass before use. $\text{C}_2\text{H}_5\text{OH}$ and all other reagents used were of anal. grade purity.

Thermostat, the temperature fluctuation ± 0.05 K, was made by ourselves. WZS-1 type of Abbe refractometer, IR-440 model infrared spectrophotometer, PE-TGS-7 thermogravimetric analyzer, and DSC-2

differential scanning calorimeter were used. The thermometer, weights and all measuring vessels used were calibrated.

Yb^{3+} was determined complexometrically with EDTA, $\text{C}_2\text{H}_5\text{OH}$ and H_2O were determined by the volatilization mass loss method. Mass losses of some known samples are given in Table 1 indicating that analytical relative errors are less than 0.3 %. $18\text{C}6$ was found from the difference subtraction method.

The semimicrophase equilibrium method used was designed by Jiang *et al.* [5]. The samples, which are 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 title system $\text{YbCl}_3 \cdot 3\text{H}_2\text{O}$ — $18\text{C}6$ — $\text{C}_2\text{H}_5\text{OH}$ at 298.15 K by the above-mentioned method. The results showed that the equilibrium of this system was reached after stirring in thermostat for 14 d.

Based on phase equilibrium data in this paper the points were selected in the 2-phase regions, corresponding to three complexes, then the samples were prepared, sealed in polyvinyl tubes, fixed in turntable and turned until equilibrium. In order to make the widest possible removal of mother solution at wet-residue, samples were separated by centrifuging, washed with ethanol and dried in different drying conditions until their mass became constant.

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Table 1. Mass Losses Data of Some Known Samples in Drying Conditions

Adding to mass/mg			Mass loss/mg		
YbCl ₃ · 3H ₂ O	18C6	C ₂ H ₅ OH	over 70—80 % H ₂ SO ₄	over 98 % H ₂ SO ₄	at 50 °C, 0.8 kPa and over P ₂ O ₅
119.50	0	1105.45	—	1106.00	—
206.10	59.70	1571.90	—	1572.00	33.60 (33.49)*
177.90	69.60	1460.60	1460.35	—	28.95 (28.84)*
106.15	82.50	848.40	848.40	17.40 (17.35)*	—

*The data in parentheses are calculated values by water mass in samples.

Table 2. Solubility and Refractive Index Data of the System YbCl₃ · 3H₂O—18C6—C₂H₅OH at 298.15 K

w _i (Complex)/%		w _i (Solution)/%		w _i (Wet-Residue)/%		Equilibrium solid phase	w _i (A) × 100 %	n _D (25 °C)
A	C	A	C	A	C		w _i (A) + w _i (B)	
—	—	49.85	50.15	—	—	A	100.00	1.4285
55.59	43.76	48.80	50.22	—	—	A	98.03	1.4269
55.34	40.07	47.93	49.97	68.70	20.60	A+I	95.80	1.4320
50.02	44.86	44.93	54.17	68.00	17.00	I	98.04	1.4145
50.06	44.09	40.26	58.93	58.74	31.15	I	98.03	1.4139
49.25	44.13	37.46	61.64	58.04	30.75	I	97.65	1.4039
45.98	47.95	35.46	63.40	59.48	28.74	I	96.88	1.4085
42.08	51.08	36.10	61.83	61.60	21.38	I + II	94.58	1.3943
39.83	53.41	33.06	65.00	53.43	29.97	II	94.46	1.3932
38.69	54.05	30.49	67.00	56.93	22.87	II	93.82	1.3893
33.26	59.98	25.36	72.32	57.24	23.46	II	92.52	1.3800
27.06	66.65	20.59	76.36	43.17	42.43	II	87.10	1.3780
32.64	55.18	20.15	74.25	51.30	27.06	II + III	78.25	1.4068
—	—	20.10	74.27	38.85	37.89	II + III	78.12	1.4068
28.45	42.50	12.65	82.98	36.22	38.29	III	74.32	1.4015
25.84	59.15	12.36	83.25	37.88	37.98	III	73.79	1.3950
19.56	65.55	6.10	89.40	22.90	59.09	III	57.55	1.3800
19.53	63.34	4.13	90.04	28.89	47.01	III	41.46	1.3805
15.54	67.88	3.06	88.83	31.60	41.38	III	27.39	1.3852
11.56	67.11	2.34	81.36	31.62	38.29	III	12.55	1.3883
9.74	57.08	1.92	68.48	30.62	31.88	III	6.10	1.4023
11.44	41.68	1.88	50.62	28.82	25.07	III	3.81	1.4108
10.06	35.33	1.75	41.57	29.89	20.01	III	3.00	1.4168
14.70	22.45	1.35	29.56	28.03	15.35	III	1.95	1.4275
—	—	0.00	11.12	—	—	B	0.00	1.4480

A = YbCl₃ · 3H₂O, B = 18C6, C = C₂H₅OH.

RESULTS AND DISCUSSION

The solubility and refractive index data of the system YbCl₃ · 3H₂O—18C6—C₂H₅OH at 298.15 K are presented in Table 2.

The solubility diagram (a) and refractive index curve (b) of saturated solutions of the system YbCl₃ · 3H₂O—18C6—C₂H₅OH at 298.15 K are presented in Fig. 1. The curves are exactly correspondent. The solubility curve ABCDE of this system is made of four portions, corresponding to the solid phases: YbCl₃ · 3H₂O, Complex I — 3YbCl₃ · 18C6 · 9H₂O · C₂H₅OH, Complex II — 2YbCl₃ · 18C6 · 6H₂O · C₂H₅OH, and complex III — YbCl₃ · 18C6 · 3H₂O, respectively; B is eutonic point to YbCl₃ · 3H₂O with complex I; C complex I with complex II; D complex II with complex III. Points A and F denote the solu-

bility of the YbCl₃ · 3H₂O and 18C6, respectively, at 298.15 K. It is very difficult to determine the eutonic point of complex III with 18C6 owing to the viscosity of corresponding saturated solution being extremely large. But as can be seen from Fig. 1, the solubility curve corresponding to the solid phase 18C6 would be very short and the 2-phase region of 18C6 is quite small, this also ruled out the possibility of formation of other stoichiometric complex. This system is invariant at B, C, D 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; there are three stoichiometric complexes formed in this system. Their compositions are given in Table 3. The complex I and complex II are incongruently soluble in C₂H₅OH, while the complex III is congruently soluble in C₂H₅OH.

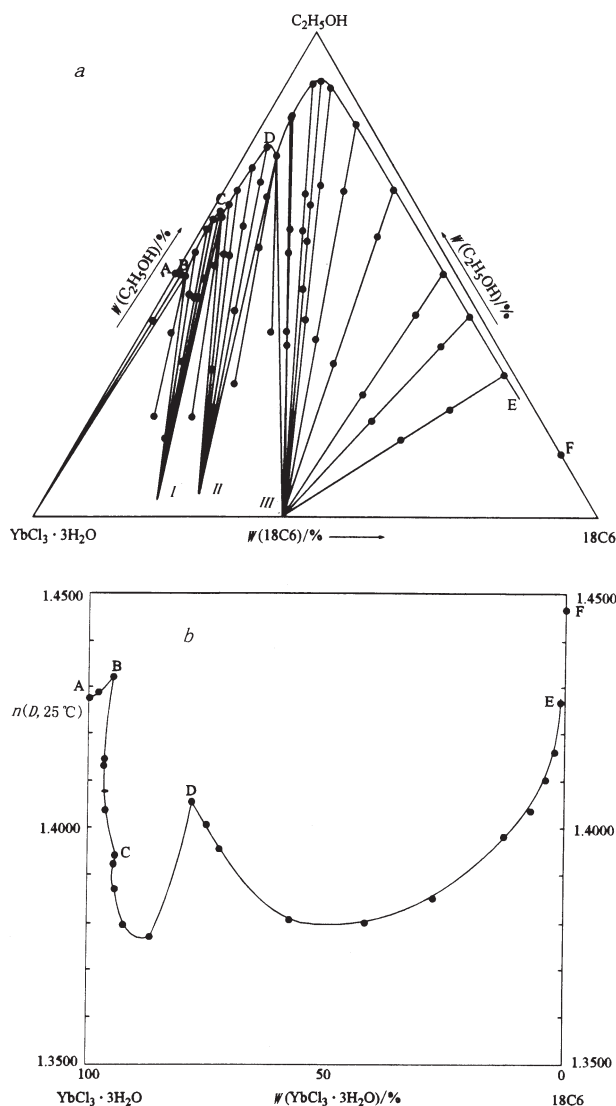


Fig. 1. Solubility diagram (a) and refractive index curve (b) of saturated solutions of the ternary system $\text{YbCl}_3 \cdot 3\text{H}_2\text{O}$ — $18\text{C}6$ — $\text{C}_2\text{H}_5\text{OH}$ at 298.15 K.

The behaviour of water in this system during equilibrium was examined and the results show that the mole ratio, $n(\text{H}_2\text{O})/n(\text{YbCl}_3)$, is always 3 : 1, no matter whether it is in liquid or solid phase. This goes a step further to indicate that the above-mentioned results of phase equilibrium are reliable.

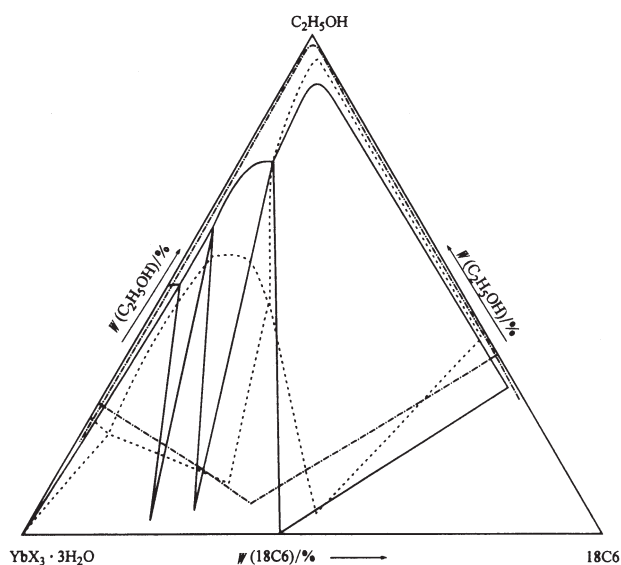


Fig. 2. Comparison of solubility diagrams of the $\text{LnX}_3 \cdot 3\text{H}_2\text{O}$ — $18\text{C}6$ — $\text{C}_2\text{H}_5\text{OH}$ systems at 298.15 K. — $\text{YbCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{Yb}(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$, - · - $\text{Yb}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$.

The influence of lanthanide ions on complex formation has been examined. Comparing the $\text{YbCl}_3 \cdot 3\text{H}_2\text{O}$ — $18\text{C}6$ — $\text{C}_2\text{H}_5\text{OH}$ system at 298.15 K with the $\text{LnCl}_3 \cdot 3\text{H}_2\text{O}$ — $18\text{C}6$ — $\text{C}_2\text{H}_5\text{OH}$ ($\text{Ln} = \text{La}$ [1], Pr [2], Gd [3]) systems at 298.15 K (Table 4), it is found that the solubility diagrams of these systems are quite different. The difference of lanthanide ions of $\text{LnCl}_3 \cdot 3\text{H}_2\text{O}$ does affect the kind and stoichiometric ratio, as well as the size of the phase regions of complexes formed in these systems, and many complexes formed in these systems are incongruently soluble in $\text{C}_2\text{H}_5\text{OH}$. This may be an important reason why the solid complexes of rare earth chloride with crown ether have rarely been reported.

Comparing the $\text{YbCl}_3 \cdot 3\text{H}_2\text{O}$ — $18\text{C}6$ — $\text{C}_2\text{H}_5\text{OH}$ system at 298.15 K with the $\text{Yb}(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ [6]/ $\text{Yb}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ [7]— $18\text{C}6$ — $\text{C}_2\text{H}_5\text{OH}$ systems at 298.15 K (Fig. 2), it is found that there are three kinds of complexes formed in the studied system, and two kinds of complexes: $\text{Yb}(\text{ClO}_4)_3 \cdot 18\text{C}6 \cdot 3\text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH}$ and $\text{Yb}(\text{ClO}_4)_3 \cdot 2(18\text{C}6) \cdot 3\text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH}$ are formed in the $\text{Yb}(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ — $18\text{C}6$ — $\text{C}_2\text{H}_5\text{OH}$ system, while only one complex, namely: $\text{Yb}(\text{NO}_3)_3 \cdot$

Table 3. Chemical Composition and Mole Ratio of Complexes

Complex	$w_i(\text{Complex in solubility diagram})/\%$			Mole ratio of complex				Soluble congruence			
	$\text{YbCl}_3 \cdot 3\text{H}_2\text{O}$	$18\text{C}6$	$\text{C}_2\text{H}_5\text{OH}$	$n(\text{YbCl}_3)$	$n(18\text{C}6)$	$n(\text{H}_2\text{O})$	$n(\text{C}_2\text{H}_5\text{OH})$				
I	76.33	20.16	3.51	3	:	1	:	9	:	1	Incongruent
II	68.25	27.04	4.71	2	:	1	:	6	:	1	Incongruent
III	55.80	44.20	—	1	:	1	:	3			Congruent

Table 4. Comparison of Main Results of the RECl₃ · 3H₂O—18C6—C₂H₅OH System at 298.15 K

Ternary system	Complexes formed in the ternary system		
	Species	Composition	Soluble congruence
YbCl ₃ · 3H ₂ O—18C6—C ₂ H ₅ OH	3	3YbCl ₃ · 18C6 · 9H ₂ O · C ₂ H ₅ OH	Incongruent
		2YbCl ₃ · 18C6 · 6H ₂ O · C ₂ H ₅ OH	Incongruent
		YbCl ₃ · 18C6 · 3H ₂ O	Congruent
GdCl ₃ · 3H ₂ O—18C6—C ₂ H ₅ OH	2	3GdCl ₃ · 18C6 · 9H ₂ O · C ₂ H ₅ OH	Incongruent
		GdCl ₃ · 18C6 · 3H ₂ O	Congruent
PrCl ₃ · 3H ₂ O—18C6—C ₂ H ₅ OH	3	2PrCl ₃ · 18C6 · 6H ₂ O	Incongruent
		4PrCl ₃ · 3(18C6) · 12H ₂ O	Congruent
		PrCl ₃ · 18C6 · 3H ₂ O	Congruent
LaCl ₃ · 3H ₂ O—18C6—C ₂ H ₅ OH	3	3LaCl ₃ · 18C6 · 9H ₂ O · C ₂ H ₅ OH	Incongruent
		2LaCl ₃ · 18C6 · 6H ₂ O · C ₂ H ₅ OH	Incongruent
		LaCl ₃ · 18C6 · 3H ₂ O	Congruent

Table 5. Analytical Results of Compositions of Complexes

Drying condition	<i>w_i</i> / %*			Composition of obtained complexes
	YbCl ₃	18C6	H ₂ O	
98 % H ₂ SO ₄	66.28 (66.24)	20.80 (20.84)	9.01 (9.04)	3YbCl ₃ · 18C6 · 9H ₂ O (<i>IV</i>)
80 % H ₂ SO ₄	59.86 (60.00)	28.51 (28.39)	11.59 (11.61)	2YbCl ₃ · 18C6 · 6H ₂ O (<i>V</i>)
70 % H ₂ SO ₄	46.77 (46.74)	41.18 (41.22)	9.05 (9.04)	YbCl ₃ · 18C6 · 3H ₂ O (<i>III</i>)
98 % H ₂ SO ₄	59.00 (58.89)	41.05 (41.11)	0	YbCl ₃ · 18C6 (<i>VI</i>)

*Calculated values in parentheses.

Table 6. Main IR Absorptions and Relative Ratio Values of their Absorbances for the Solid Complexes and 18C6

Compound	<i>t</i> (CH ₂)	$\tilde{\nu}(\nu_s(\text{C—O—C}))$	$\tilde{\nu}(\nu_{as}(\text{C—O—C}))$	<i>r</i> (CH ₂)	Relative ratio values of the absorbances
18C6	1278	990	1120	855	1:1.29:1.18:1.25
<i>III</i>	1300	957	1098	836	1:0.65:0.88:0.86
<i>IV</i>	1285	955	1095	815	1:0.81:0.95:0.88
<i>V</i>	1295	955	1096	824	1:0.87:0.96:0.90
<i>VI</i>	1303	960	1105	830	1:0.82:0.93:0.76

18C6 · 3H₂O · C₂H₅OH, which is congruently soluble in C₂H₅OH, is formed in the Yb(NO₃)₃ · 3H₂O—18C6—C₂H₅OH system.

It is a matter of common observation that nitrate ions behave as bidentate ligands with strong coordination ability, while chloride and perchlorate ions behave as unidentate or free ligands with weak coordination ability. The above-mentioned differences of phase behaviour for three compared ternary systems are owing to the differences of anions of LnX₃ · 3H₂O.

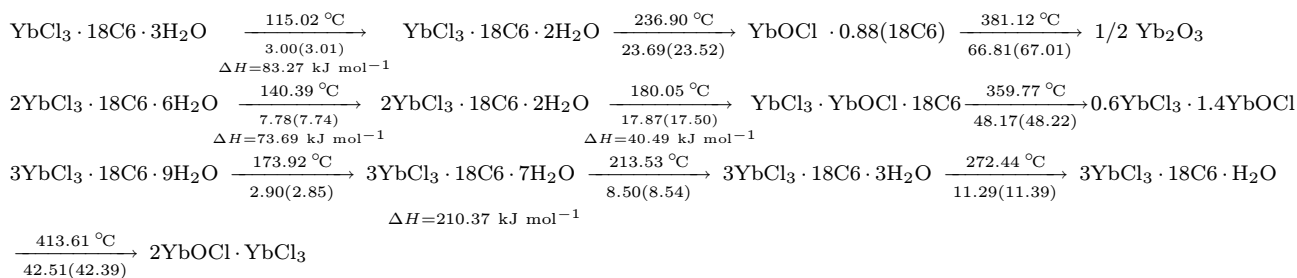
The analytical results of compositions of the solid complexes obtained at different drying conditions are in Table 5.

Main IR absorptions and relative ratio values of their absorbances for the solid complexes and 18C6 are reported in Table 6.

As can be seen, after formation of the corresponding complexes, obvious shifts of 7—40 cm⁻¹ in the vibrational bands due to the 18C6 and changes of rela-

tive ratio of their absorbance were observed compared to those for the free crown 18C6. These results indicate that the crown oxygen atoms are coordinated to the Yb³⁺ ion. Broad bands appearing at 3360—3380 cm⁻¹ and vibrational bands at 1621—1631 cm⁻¹ provide an evidence for the existence of water molecules in these complexes. For the solid complex YbCl₃ · 18C6 · 3H₂O, provided all the six crown oxygen atoms, one chlorine atom “above” the crown, and two water molecules “below” are coordinated to the Yb³⁺ ion, which is a reasonable assumption in view of the published crystal structure of lanthanide complexes with 18C6 [8], the coordination number of the Yb³⁺ ion in this complex is 9.

The thermal decomposition mechanism of the complexes *III—V* may be determined according to TG curve as follows. Comparison of the found numerical values (mass loss/%) with the calculated ones was done in the following equations.



where the temperatures are corresponding to one of DTG peaks at each step of thermal decomposition. According to the DSC of the solid complexes, the enthalpies of some steps during the decompositions, which were given in the above-mentioned equations, were obtained for three solid complexes.

In order to examine the decomposition mechanism mentioned above, we have identified the intermediates during the thermal decomposition of complexes by IR spectra. The $\tilde{\nu}(\nu_s(\text{C—O—C}))$ at 952—958 cm^{-1} and $\tilde{\nu}(\nu_{as}(\text{C—O—C}))$ at 1095—1103 cm^{-1} in IR spectra of the intermediates provide an evidence for the existence of coordination of the 18C6 molecules to the Yb^{3+} ion in these intermediates. As can be seen from the equations, our suggestion of decomposition mechanism of complexes confirms the reality.

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