

The Phase System CsCl—SmCl₃—CH₃COOH (*w* = 0.40)—H₂O at 30 °C

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The isothermal solubility of the system CsCl—SmCl₃—CH₃COOH (*w* = 0.40)—H₂O at 30 °C was determined and the phase diagram was constructed. A compound, 2CsCl · SmCl₃ · 4H₂O, was obtained from the system. Using this compound as a starting material, the patterns for synthesizing Cs₂SmCl₅, Cs₃Sm₂Cl₉, and Cs₃SmCl₆ are proposed.

The phase diagram of the system CsCl—SmCl₃ in which CsSm₂Cl₇, CsSmCl₅, and Cs₃SmCl₆ were observed has been investigated [1]. However, it is difficult to obtain Cs₂SmCl₅ and CsSm₂Cl₇ since they are existing with an incongruently melting point at 561 °C. CsPr₂Cl₇, Cs₂LuCl₅, Cs₃Lu₂Cl₉, and Cs₃LuCl₆ were synthesized by using CsCl, HCl(aq), and RECl₃ · *n*H₂O or RE₂O₃ (RE refers to rare-earth element) as the starting materials [2]. We studied the systems CsCl—RECl₃ (RE = La [3], Pr [4], Sm [5], and Gd [6])—HCl—H₂O and CsCl—RECl₃ (RE = La [3], Pr [4], and Gd [6])—CH₃COOH—H₂O. The system CsCl—SmCl₃—HCl—H₂O, in which only 2CsCl · SmCl₃ · 4H₂O was observed, was used as a guide to synthesize Cs₂SmCl₅ but it was of little value in acquiring CsSm₂Cl₇. The result that CsCl · LaCl₃ · 2H₂O is absent in the system CsCl—LaCl₃—HCl—H₂O but present in the system CsCl—LaCl₃—CH₃COOH—H₂O meant that CsSm₂Cl₇ might be obtained in the system CsCl—SmCl₃—CH₃COOH—H₂O. This study was conducted at 30 °C and the obtained results are compared to the previously reported systems [3—6]. These comparisons are made to show that physico-chemical properties of LaCl₃ · 7H₂O, PrCl₃ · 6H₂O, SmCl₃ · 6H₂O, and GdCl₃ · 6H₂O in aqueous solution of HCl and CsCl are similar to those in aqueous solution of CH₃COOH and CsCl, respectively. Based on the compound found in the system CsCl—SmCl₃—CH₃COOH (*w* = 0.40)—H₂O at 30 °C, the patterns for synthesizing Cs₂SmCl₅, Cs₃Sm₂Cl₉, and Cs₃SmCl₆ are proposed.

EXPERIMENTAL

CsCl and CH₃COOH were anal. grade chemicals made in China. SmCl₃ · 6H₂O was crystallized from a solution of Sm₂O₃ (*w* = 0.9999) in hydrochloric acid. CsCl, SmCl₃ · 6H₂O, and CH₃COOH aqueous solution was sealed in a reaction bottle which was agitated by an electrical agitator. The concentration of CH₃COOH in liquid phases was monitored with chemical analysis and concentrated CH₃COOH was added when its mass percentage in liquid phases was not 0.38—0.42 in the first 5 days. Continuous agitation of the reaction bottle for another 7 days with no apparent change of the solid phases is considered as an acceptable criterion for equilibrium.

After equilibrium, the liquid phase sample and wet residue sample were taken for chemical analysis and the composition of the solid phase was confirmed by the Schreinemakers method. The observed compound was characterized by thermal-chemical analysis, micropolariscope and X-ray diffraction method.

X-Ray powder diffraction: Rigaka D/max-2400. Cu target. Scanning rate is 8° min⁻¹ and scanning scope 60°

TG-DTG and DTA measurement: Setaram TGD-TA92. N₂ atmosphere and heating rate 10 °C min⁻¹

RESULTS AND DISCUSSION

The saturation compositions of solution and residues for the system CsCl—SmCl₃—CH₃COOH (*w* = 0.40)—H₂O at 30 °C are presented in Table 1.

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Table 1. Solubility of Saturated Solutions of the CsCl—SmCl₃—CH₃COOH ($w = 0.40$)—H₂O System at 30 °C

No.	$w_i(\text{solution})/\%$					$w_i(\text{residues})/\%$					Solid phase*
	Composition in the tetrahedron			Composition on the triangle		Composition in the tetrahedron			Composition on the triangle		
	SmCl ₃	CH ₃ COOH	CsCl	SmCl ₃	CsCl	SmCl ₃	CH ₃ COOH	CsCl	SmCl ₃	CsCl	
1	27.84	42.00	0.00	48.00	0.00	—	—	—	—	—	A
2	24.21	43.74	3.41	43.03	6.06	50.00	18.16	1.72	61.09	2.10	A
3	24.46	40.99	6.59	41.45	11.17	48.38	18.62	3.46	59.45	4.25	A
4	21.24	41.66	11.39	36.40	19.52	52.85	14.07	4.19	61.50	4.88	A
5	22.08	40.89	12.35	37.35	20.89	52.64	13.64	4.89	60.95	5.66	A
6	22.76	37.50	12.38	36.42	19.80	49.07	14.18	8.91	57.18	10.38	A + B
7	23.87	36.00	12.87	37.29	19.97	40.47	18.94	13.85	49.93	17.09	A + B
8	22.80	37.61	11.99	36.54	19.21	38.24	16.39	20.52	45.74	24.54	A + B
9	19.46	36.68	16.73	30.73	26.42	30.32	16.01	32.16	36.10	38.25	B
10	15.22	41.50	26.91	26.01	46.00	25.97	13.45	41.60	30.00	48.07	B
11	8.69	40.59	28.75	14.63	48.39	23.14	18.75	40.04	28.48	49.28	B
12	7.20	42.00	38.28	10.59	56.29	10.13	5.50	75.07	10.72	79.43	B + C
13	2.90	44.67	34.99	5.23	62.15	4.71	23.35	61.49	6.14	80.22	C
14	0.00	40.90	40.14	0.00	67.92	—	—	—	—	—	C

*A = SmCl₃ · 6H₂O, B = Cs₂SmCl₅ · 4H₂O, C = CsCl.

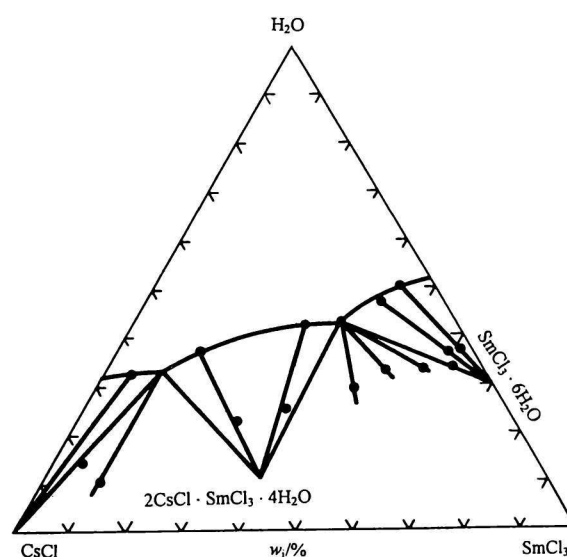
Table 2. The Compounds Existing in the CsCl—RECl₃ (RE = La, Pr, Sm, and Gd)—CH₃COOH—H₂O Systems

System	$x(\text{Cs})$	$x(\text{RE}) = 1$	1	$x(\text{Cs})$	$x(\text{RE}) = 2$	1	$x(\text{Cs})$	$x(\text{RE}) = 3$	1
CsCl—LaCl ₃ —CH ₃ COOH—H ₂ O					2CsCl · LaCl ₃ · 2H ₂ O			3CsCl · LaCl ₃ · 3H ₂ O	
CsCl—PrCl ₃ —CH ₃ COOH—H ₂ O		CsCl · PrCl ₃ · 6H ₂ O						3CsCl · PrCl ₃ · 7H ₂ O	
CsCl—SmCl ₃ —CH ₃ COOH—H ₂ O					2CsCl · SmCl ₃ · 4H ₂ O				
CsCl—GdCl ₃ —CH ₃ COOH—H ₂ O					2CsCl · GdCl ₃ · 7H ₂ O				

The phase diagrams of the systems CsCl—SmCl₃—CH₃COOH—H₂O at 30 °C and CsCl—SmCl₃—HCl—H₂O [5] are plotted in Figs. 1 and 2, respectively. Table 2 gives the types of compounds determined in all the studied systems.

The phase diagram of the CsCl—SmCl₃—CH₃COOH ($w = 0.40$)—H₂O system at 30 °C consists of three solubility curves corresponding to solid phases CsCl, 2CsCl · SmCl₃ · 4H₂O, and SmCl₃ · 6H₂O, respectively. The compound, 2CsCl · SmCl₃ · 4H₂O (light yellow), is obtained as moisture-sensitive powder and is congruently soluble in water. Observed by micropolariscope, the compound crystallizes as a homogeneous body with particular geometric shape and belongs to diaxialite(-). The results of X-ray powder diffraction pattern, TG-DTG and DTA measurements of the compound are the same as those of the system CsCl—SmCl₃—HCl—H₂O [5] and are not presented here. CsSm₂Cl₇, CsSmCl₄, and Cs₃SmCl₆ are not observed in the system.

Comparing the CsCl—SmCl₃—CH₃COOH ($w = 0.40$)—H₂O system at 30 °C with the CsCl—SmCl₃—HCl ($w = 0.13$)—H₂O system at 25 °C [5] (Fig. 2), the phase behaviour of 2CsCl · SmCl₃ · 4H₂O in the CsCl—SmCl₃—HCl ($w = 0.13$)—H₂O system and the CsCl—SmCl₃—CH₃COOH ($w = 0.40$)—H₂O system

**Fig. 1.** Phase diagram of the CsCl—SmCl₃—CH₃COOH ($w = 0.40$)—H₂O system at 30 °C.

is nearly the same. It is congruently soluble in water in both the systems, in spite of the phase area of 2CsCl · SmCl₃ · 4H₂O in the CsCl—SmCl₃—CH₃COOH ($w = 0.40$)—H₂O system is slightly bigger than that in

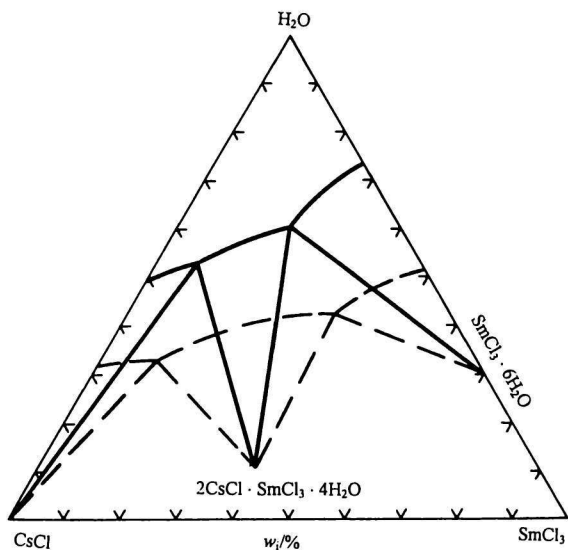


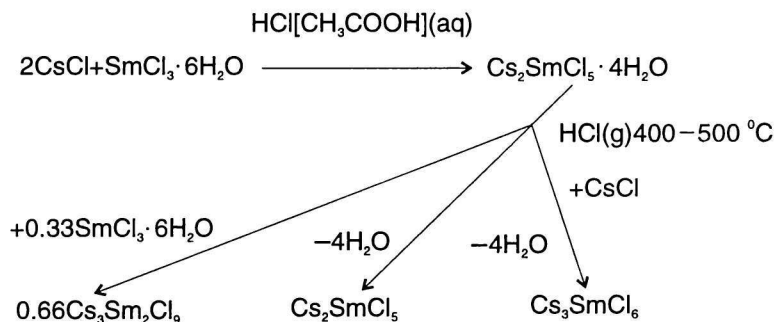
Fig. 2. Phase diagram of the CsCl—SmCl₃—CH₃COOH ($w = 0.40$)—H₂O system (---) at 30°C and the CsCl—SmCl₃—HCl ($w = 0.13$)—H₂O system (—) at 25°C.

the CsCl—SmCl₃—HCl ($w = 0.13$)—H₂O system. It is indicated that CH₃COOH could be used as another

medium to obtain 2CsCl·SmCl₃·4H₂O.

In the previous study of the phase systems CsCl—RECl₃ (RE = La [3], Pr [4], Sm [5], and Gd [6])—HCl ($w = 0.13$)—H₂O at 25°C, the two-sub-group effect of the light rare-earth element which is one of the parts of the “Tetrad effect” [7] has been discussed. Dividing the compounds discovered in the CsCl—RECl₃ (RE = La [3], Pr [4], Sm [5], and Gd [6])—CH₃COOH—H₂O systems at 30°C (Table 2) into 4 types, the group effect of Sm and Gd is obvious, while that of La and Pr is not clear. Presence of 2CsCl·LaCl₃·2H₂O in the CsCl—SmCl₃—CH₃COOH—H₂O system and absence in the CsCl—SmCl₃—HCl—H₂O system might be used as a guide to synthesize different kinds of compounds from different systems.

In Meyer's [2] study, Cs₂LuCl₅, Cs₃Lu₂Cl₉, and Cs₃LuCl₆ were prepared by using Cs₂LuCl₅·H₂O as the intermediate product. The compound Cs₂SmCl₅·4H₂O, which was obtained in both CsCl—SmCl₃—CH₃COOH—H₂O and CsCl—SmCl₃—HCl—H₂O systems, was accordingly assumed to be an intermediate product for preparation of Cs₂SmCl₅, Cs₃Sm₂Cl₉, and Cs₃SmCl₆. By imitating the Meyer reaction, the syntheses of Cs₂SmCl₅, Cs₃Sm₂Cl₉, and Cs₃SmCl₆ are proposed as follows



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