Phase Diagrams of YCl_3–KCl, YCl_3–NaCl, and YCl_3–KCl·NaCl Systems, and Densities of Their Molten Mixtures

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(Received June 7, 1973)

YCl_3 has been prepared with Y_2O_3 and NH_4Cl, and the optimum conditions for chlorination have been determined. The YCl_3 salt obtained was purified to a pure YCl_3 crystal by sublimation. Phase diagrams of binary YCl_3–KCl and YCl_3–NaCl system, and liquidus curve diagram of quasi-binary YCl_3–KCl·NaCl system have been determined with the use of the purified YCl_3 crystal. Densities of YCl_3 and the mixtures in molten state were measured dilatometrically, and represented by empirical formulas as a function of temperature. From the results thermal expansion coefficients and molar expansibilities of the molten YCl_3 and the molar volumes of molten mixtures were calculated.

YCl_3 can be prepared by heating a mixture of Y_2O_3 and NH_4Cl:

$$Y_2O_3 + 6NH_4Cl = 2YCl_3 + 6NH_3 + 3H_2O \quad (1)$$

Since the product contains H_2O owing to the hygroscopic property of YCl_3, if the reaction temperature is too high, yttrium oxychloride is produced by the reaction of YCl_3 and H_2O, thus reducing the yield of YCl_3. In the present experiment the optimum conditions for the chlorination were determined. The YCl_3 salt was purified to a pure YCl_3 crystal by sublimation. This was used for the determination of phase diagrams and the measurement of densities of the YCl_3 and the mixture systems in molten state. Measurements of melting and transition points were carried out by differential thermal analysis. The dilatometer method was used in the measurements of densities.

Experimental

Preparation of YCl_3. A mixture of Y_2O_3 and NH_4Cl in a glass test tube of standard size was heated for a certain time in an electric furnace. The yields of YCl_3 were determined by chemical analysis of reaction products obtained under various conditions of temperature, time, and mixing ratio of Y_2O_3 and NH_4Cl. When the reaction product is treated with water purified by ion-exchange resins, YCl_3 only is dissolved in the water, but not yttrium oxychloride and Y_2O_3. The precipitate obtained by filtration of the solution was separately dissolved in the hot dilute hydrochloric acid. The amounts of Y^{+3} ions contained in both solutions were determined by the titration with EDTA solution. The yield of YCl_3 can be obtained by

$$\eta = [A/(A+B)] \times 100 \quad (\%)$$

where A is the amount of YCl_3 contained in the filtrate, and B the amount of YCl_3 contained in the solution from the filter cake. The Y_2O_3 used as starting material was 99.9% in purity (Shin-Etsu Chem. Ind. Co. Ltd., Japan: Found: Tb_4O_7, <0.003; Dy_2O_3, 0.030; Fe, 0.0003; Cu, 0.00002%). NH_4Cl(A.R. grade) was dried at about 120 °C for several hours.

Purification of YCl_3. Purification of YCl_3 is necessary since it still contains a small amount of water and NH_4Cl. Purification was carried out by sublimation in a vacuum.

Differential Thermal Analysis. Measurements were carried out from the cooling curve of the molten sample in demoistured argon gas, α-Al_2O_3 powder being used as a reference material. The cooling rates were 15 °C/min at 800 °C and 13 °C/min at 500 °C.

Measurements of Densities. The densities of the liquid chlorides were measured dilatometrically with a transparent silica dilatometer. The meniscus of molten salt was read with a cathetometer. This method was checked by measuring the densities of KCl and NaCl, the result being in good agreement with the data in literature.[1]

Results and Discussion

Preparation of YCl_3. The high yield of YCl_3 in the chlorination of Y_2O_3 makes it necessary to add an excess amount of NH_4Cl as compared with the theoretical amount in Eq. (1). The dependence of reaction time for the yield of YCl_3 at 300 °C is shown in Fig. 1, in which the curves a, b, and c are the results for the reactions with the mixtures of 1.32, 1.72, and 2.13 times the theoretical amount of NH_4Cl in Eq. (1), respectively. For curve a (1.32 times theoretical amount of NH_4Cl), the yield of YCl_3 was less than about 70%, but in the others very high yields were obtained. In cases where a more excess amount of NH_4Cl was contained the reaction rates were greater.

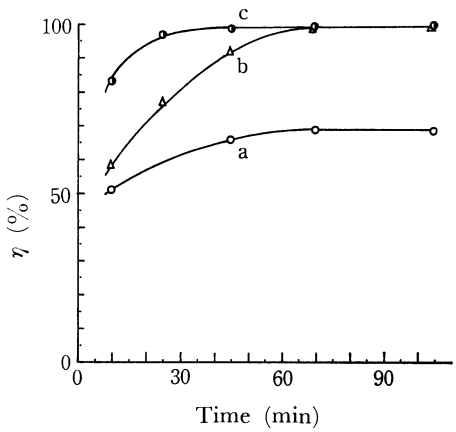

Fig. 1. Dependences of reaction time for the yield of YCl_3 at 300 °C; a: reaction of mixture containing 1.32 times of NH_4Cl, b: 1.72 times, c: 2.13 times.

The dependence of reaction temperature for the yield of YCl_3 in the reaction with 1.72 times the theoretical amount of NH_4Cl is shown in Fig. 2, in which the curves A, B, C, D, and E are the results for the reactions at 200, 250, 300, 350, and 400 °C, respectively. In the reaction at 200 °C, YCl_3 was not formed. The reactions at 350 and 400 °C proceeded rapidly,

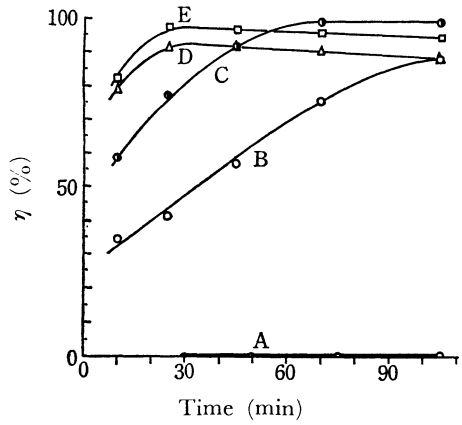

Fig. 2. Dependences of reaction temperature for the yield of YCl_3 in reactions of mixtures containing 1.72 times of NH_4Cl; A: reaction at 200 °C, B: 250 °C, C: 300 °C, D: 350 °C, E: 400 °C.

but the yields of YCl_3 decreased a little after a longer reaction time than 30 min. The tendency might indicate that the yttrium oxychloride was produced from YCl_3 and H_2O in the reaction product due to the high reaction temperature. This was also anticipated by Wendlandt[2] from the results of thermal analysis for YCl_3 containing H_2O.

It is preferable to carry out the reaction under the following optimum conditions for the chlorination of Y_2O_3 with NH_4Cl: reaction temperature 300 °C; addition to Y_2O_3 of 1.7 times or more the theoretical amount of NH_4Cl in Eq. (1); reaction time 70 min or more.

Purification of YCl_3. The maximum yield of YCl_3 crystal in sublimation, obtained when the sublimation temperature was 950—1050 °C, was about 50% after 7 hours. The purified YCl_3 crystal was completely soluble in water, the atomic ratio of Y and Cl being 1 : 3.01. The mp of this crystal was 714 and 717 °C in cooling and heating measurements, respectively, by DTA analysis. The contents of metallic impurities in this crystal are given in Table 1.

Table 1. Contents of metallic impurities in YCl_3 crystal[a]

Element	Content (ppm)	Element	Content (ppm)
La	5	Yb	< 1
Ce	<30	Lu	<10
Pr	<10	Mg	< 1
Nd	<10	Al	< 5
Sm	<10	Si	50
Eu	< 1	V	< 5
Gd	<10	Mn	< 1
Tb	< 5	Fe	5
Dy	60	Ni	< 5
Ho	<10	Cu	< 1
Er	< 5	Sn	< 5
Tm	< 5		

a) Method of analysis: Spectrographic; M. Sato, H. Matsui, and T. Matsubara, *Bunseki Kagaku*, **20**, 215 (1971).

Phase Diagram. Phase diagrams of YCl_3–KCl, YCl_3–NaCl systems and the liquids curve diagram of quasi-binary YCl_3–KCl·NaCl system are shown in Figs. 3, 4, and 5, respectively. In the YCl_3–KCl system, two intermediate compounds ($3YCl_3$·KCl and YCl_3·3KCl), one peritectic point(552 °C, 74 mol% YCl_3), 2 eutectic points(435 °C, 44 mol% YCl_3 and 685 °C, 15 mol% YCl_3), and a polymorphic transition point(367 °C) in solid range between the intermediate compounds were observed.

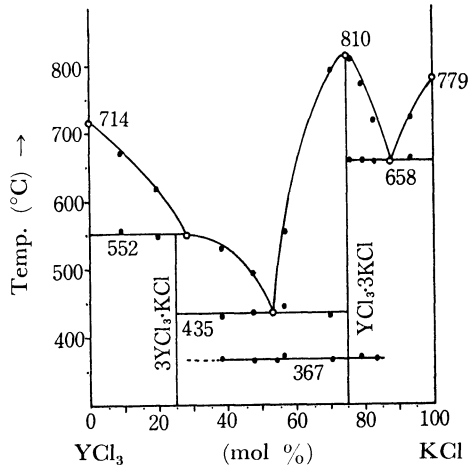

Fig. 3. Phase diagram of YCl_3-KCl system.

This is in fairly good agreement with the diagram given by Korshunov and Drobot,[3] but not with that by Su and Ch'iu.[4] In the YCl_3–NaCl system, one intermediate compound (YCl_3·3NaCl), one peritectic point (556 °C, 33 mol% YCl_3), and one eutectic point (389 °C, 50 mol% YCl_3) were observed. In this system, the intermediate compound NaCl·$9YCl_3$ reported by Su and Ch'iu[4] was not observed.

We see in Fig. 5 that the YCl_3–KCl·NaCl system has 2 minimum points (409 °C, 57 mol% YCl_3 and 600 °C, 86 mol% YCl_3), and one maximum point (632 °C, 76 mol% YCl_3).

Density of Molten YCl_3. The measurement of density of the molten YCl_3 was performed in the range

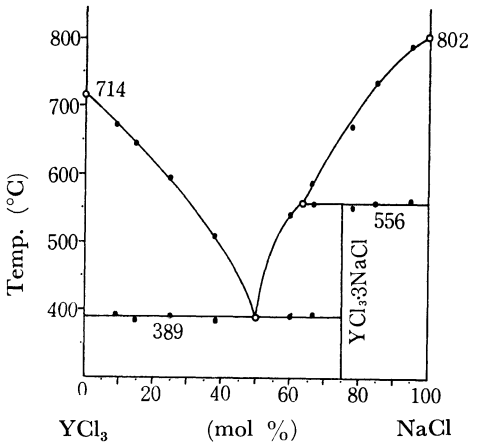

Fig. 4. Phase diagram of YCl_3-NaCl system.

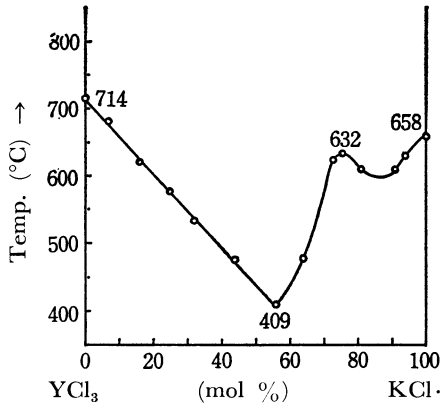

Fig. 5. Liquidus curve diagram of YCl_3-KCl·NaCl (e.m.) system.

809—1005 °C with the use of the method of least squares. The following empirical formula was obtained as a function of temperature;

$$d = 2.9226 - 4.594\times10^{-4}\,t,$$

where d is the density of molten YCl_3 in g/cm³, and t the temperature in °C. Since the density change of the molten salt with temperature is linear, the density of the molten YCl_3 at a mp of 714 °C could be calculated by extrapolation. The density of the molten YCl_3 at mp is 2.595 g/cm³. The volume change of YCl_3 on melting, calculated from the density data at room temperature (2.61 g/cm³), since the thermal expansion of the solid is much smaller than that of the liquid, was +0.594% for the solid volume. This is much smaller than the given values of $PrCl_3$, $NdCl_3$, and $GdCl_3$.[5]

Coefficients of Thermal Expansion of Molten YCl_3. The expansivity and molar expansibility of molten YCl_3 under atmospheric pressure were calculated by combining the formula with the equation

$$\alpha = -(1/d)(\partial d/\partial t)_p \qquad (2)$$

where α is the expansivity in /°C under the pressure p. The molar expansibility is equal to αV, where V is the molar volume of molten YCl_3. The values of the expansivity and molar expansibility are given in Table 2.

Table 2. Expansivity and molar expansibility of molten YCl_3

Temp. (°C)	Expansivity (/°C)	Molar expansibility (cm³/mol °C)
750	1.782×10^{-4}	1.350×10^{-2}
800	1.798×10^{-4}	1.374×10^{-2}
850	1.814×10^{-4}	1.399×10^{-2}
900	1.831×10^{-4}	1.425×10^{-2}
950	1.848×10^{-4}	1.451×10^{-2}
1000	1.865×10^{-4}	1.479×10^{-2}

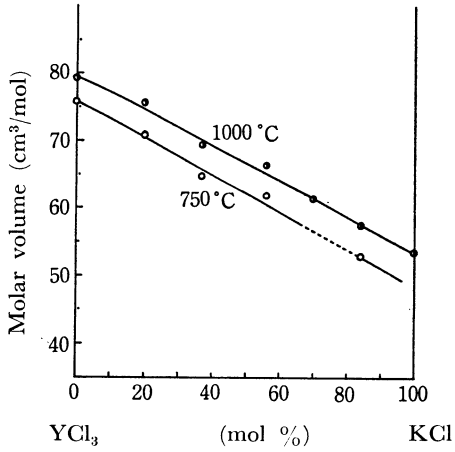

Fig. 6. Molar volume isotherm of molten YCl_3-KCl system.

Table 3. Empirical formulas of densities for molten mixtures

(a) YCl_3-KCl system

Component (mol %)		Density (d: g/cm²; t: °C)	Temp. range (°C)
YCl_3	KCl	$d=a+bt$	
80.2	19.8	$d=2.8914-6.312\times10^{-4}t$	800—1003
63.2	36.8	$d=2.7995-6.199\times10^{-4}t$	819— 990
44.4	55.6	$d=2.4823-5.594\times10^{-4}t$	800—1000
29.9	70.1	$d=2.3586-5.540\times10^{-4}t$	881— 999
15.8	84.2	$d=2.2017-5.790\times10^{-4}t$	800—1000

(b) YCl_3-NaCl system

Component (mol %)		Density (d: g/cm³; t: °C)	Temp. range (°C)
YCl_3	NaCl	$d=a+bt$	
85.0	15.0	$d=2.8784-4.515\times10^{-4}t$	812— 999
69.8	30.2	$d=2.8663-6.219\times10^{-4}t$	798—1002
59.1	40.9	$d=2.7659-5.398\times10^{-4}t$	807—1005
44.2	55.8	$d=2.5862-5.367\times10^{-4}t$	797— 997
28.1	71.9	$d=2.4230-5.264\times10^{-4}t$	807— 990
14.9	85.1	$d=2.2897-5.501\times10^{-4}t$	797— 960

(c) YCl_3-KCl·NaCl system

Component (mol%)			Density (d: g/cm³; t: °C)	Temp. range (°C)
YCl_3	KCl	NaCl	$d=a+bt$	
83.8	8.1	8.1	$d=2.8932-5.835\times10^{-4}t$	806— 932
69.2	15.4	15.4	$d=2.7918-6.142\times10^{-4}t$	809— 985
49.9	25.05	25.05	$d=2.6089-6.038\times10^{-4}t$	803— 980
27.8	36.1	36.1	$d=2.3457-5.294\times10^{-4}t$	805— 950
16.3	41.85	41·85	$d=2.2729-5.907\times10^{-4}t$	820— 995
0.0	50.0	50.0	$d=1.8865-5.470\times10^{-4}t$	815—1000

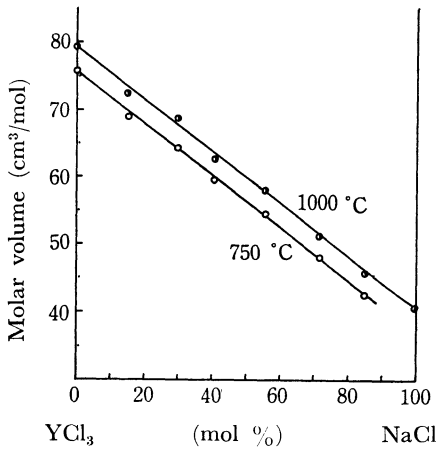

Fig. 7. Molar volume isotherm of molten YCl_3-NaCl system.

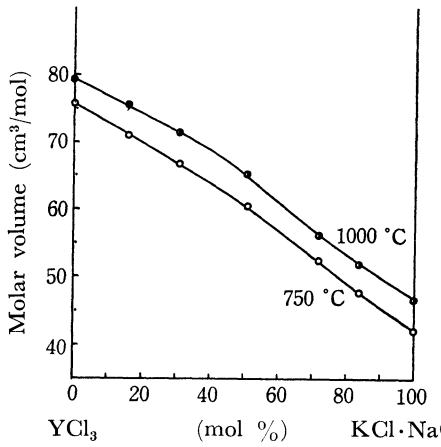

Fig. 8. Molar volume isotherm of molten YCl_3-KCl·NaCl (e.m.) system.

Densities of the Molten Mixtures. The densities of molten mixtures were measured for the various compositions in YCl_3–KCl, YCl_3–NaCl, and YCl_3–KCl·NaCl systems. The density data were treated then by the method of least-squares and represented by the empirical formulas as functions of temperature. The formulas are given in Table 3.

Molar Volume Isotherms. From the formulas in Table 3, the molar volumes of the molten mixtures were calculated by the following equation.

$$V_{mix} = \sum (X_i M_i)/d_{mix},$$

where V_{mix} is the molar volume of molten mixture in cm^3/mol, X_i the mole fraction of component i in the mixture, M_i the molecular weight of the component i in the mixture in g/mol, and d_{mix} the observed density of the molten mixture in g/cm^3. The molar volume isotherms of three molten mixture systems are shown in Figs. 6, 7, and 8.

The authors wish to thank Mr. Matsuji Sato, Shin-Etsu Chem. Ind. Co., for assistance in the analysis of materials.

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