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Densities and Molar Volumes of Molten Binary $PrCl_3$–KCl, $PrCl_3$–NaCl, $PrCl_3$–$CaCl_2$, $NdCl_3$–KCl, $NdCl_3$–NaCl, $NdCl_3$–$CaCl_2$ Systems

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Synopsis. The densities of $PrCl_3$, $NdCl_3$, $PrCl_3$–KCl, $PrCl_3$–NaCl, $PrCl_3$–$CaCl_2$, $NdCl_3$–KCl, $NdCl_3$–NaCl, and $NdCl_3$–$CaCl_2$ melts measured dilatometrically were represented by the empirical equations as functions of temperature. The molar volumes of the melts were calculated from the density data.

Densities and molar volumes of molten salts are the important properties in thermodynamic considerations, and are necessary to calculate the molar quantities. The ideal solution has the additivities of extensive properties except for entropy. Therefore, very few is known to have ideal behavior among the real mixture melts, but there are several molten mixture systems that have approximately the additive behavior for some of the extensive properties. In the previous paper, we reported on the densities and molar volume isotherms of molten YCl_3–KCl, YCl_3–NaCl, YCl_3–KCl–NaCl systems.[1] In the present experiment, the densities of 6 binary mixture systems ($PrCl_3$–KCl, –NaCl, –$CaCl_2$, and $NdCl_3$–KCl, –NaCl, –$CaCl_2$) in the molten state were measured, and the molar volume isotherm equations of these melts at 800 and 1000 °C were calculated.

Experimental

Materials. $PrCl_3$ and $NdCl_3$ were prepared by heating the respective rare-earth oxide with NH_4Cl at 350 and 370 °C, respectively, for 1.5 hr in evacuating with a rotary pump. The mixing ratio of NH_4Cl for each oxide was 2.5 times the theoretical amount. The chlorides were then purified by heating at about 850 °C *in vacuo* to remove the excess amount of NH_4Cl by sublimation. The analysis of impurities in the purified chlorides are shown in Table 1. The ratios of rare-earth and chlorine elements were 1 : 2.96 for both chlorides.

KCl, NaCl, and $CaCl_2$ were dried by heating *in vacuo* for 5 hr or more at the temperature lower by about 50 °C than the melting points of the salts.

Density Measurement. The dilatometric method was used. A dilatometer was made of transparent silica, and the volume of a dilatometer was determined by use of distilled water at room temperature because the thermal expansion coefficient of quartz is very smaller than that of molten salts. In the measurement the meniscus of melt in a dilatometer was read with a cathetometer.

TABLE 1. IMPURITIES IN $PrCl_3$ AND $NdCl_3$[a)]

$PrCl_3$		$NdCl_3$	
Element	Content (ppm)	Element	Content (ppm)
La	<50	Ce	160
Ce	<30	Pr	<30
Nd	<20	Sm	27
Sm	<20	Eu	<30

a) Fluorescent X-ray analysis.

Results and Discussion

Densities of Molten $PrCl_3$ and $NdCl_3$. Since the change in density of molten salt with increasing temperature is linear, the densities of molten $PrCl_3$ and $NdCl_3$ were represented by the following empirical equations as functions of temperature by use of the method of least squares for the density data observed.

$$PrCl_3;\ d=4.139-1.030\times10^{-3}\,t\ (850\leq t\leq1000)\qquad \sigma=0.017$$

$$NdCl_3;\ d=3.992-0.8047\times10^{-3}\,t\ (802\leq t\leq1009)\qquad \sigma=0.011$$

where d is the density of $PrCl_3$ or $NdCl_3$ melt in g/cm^3, t the temperature in °C. σ is the standard error of estimate in density equations in g/cm^3. The results were in fairly good agreement with the densities reported by Cho *et al.*[2)]

Densities of Six Binary Systems. The density equations of molten mixtures in various compositions of six binary systems are shown in Table 2.

Molar Volumes of Binary Systems. Molar volume of mixture melt is calculated by the equation, $V_{mix}=\Sigma(X_i\cdot M_i)/d_{mix}$, where V_{mix} is the molar volume of the mixture melt, X_i the mole fraction of i-th component, M_i the molecular weight, and d_{mix} the density of the melt. The molar volume isotherm of $PrCl_3$–KCl system at 800 and 1000 °C are shown in Fig. 1. For six binary systems the molar volume isotherm equations are shown in Table 3.

The phase diagrams of binary $PrCl_3$–NaCl[3)], $PrCl_3$–$CaCl_2$, $NdCl_3$–NaCl,[4)] and $NdCl_3$–$CaCl_2$[4)] systems

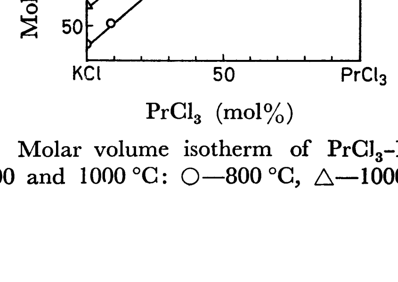

Fig. 1. Molar volume isotherm of $PrCl_3$-KCl system at 800 and 1000 °C: ○—800 °C, △—1000 °C.

TABLE 2. DENSITY EQUATIONS OF MOLTEN SYSTEMS $d=a+b\times10^{-3}t$ d: g/cm³, t: °C

System mol%	mol%	a	b $\times10^{-3}$	Temp. range (°C)	σ (g/cm³) $\times10^{-2}$
(a) $PrCl_3$-KCl					
0.0	100.0	2.011	−0.609	849—1008	0.123
8.9	91.1	2.131	−0.539	800—958	0.489
20.5	79.5	2.416	−0.571	800—1000	0.701
33.8	66.2	2.777	−0.707	803—1000	0.286
50.3	49.7	3.149	−0.761	800—1000	0.320
68.5	31.5	3.532	−0.898	800—1000	1.07
81.4	18.6	3.721	−0.874	820—1000	1.01
(b) $PrCl_3$-NaCl					
0.0	100.0	2.024	−0.573	838—1021	0.375
11.6	88.4	2.503	−0.666	840—1005	0.678
25.8	74.2	2.772	−0.610	810—1000	0.701
39.4	60.6	3.046	−0.671	830—1000	0.769
61.9	38.1	3.429	−0.708	825—1000	0.311
75.2	24.8	3.648	−0.711	820—1000	0.392
(c) $PrCl_3$-$CaCl_2$					
0.0	100.0	2.473	−0.424	825—1011	0.504
9.7	90.3	2.639	−0.487	800—1000	0.155
20.6	79.4	2.867	−0.518	800—1000	0.132
35.2	64.8	3.143	−0.586	800—1000	0.321
50.7	49.3	3.377	−0.664	800—1000	0.207
66.8	33.2	3.685	−0.820	800—1000	0.512
80.3	19.7	3.844	−0.793	820—1000	0.527

System mol%	mol%	a	b $\times10^{-3}$	Temp. range (°C)	σ (g/cm²) $\times10^{-2}$
(d) $NdCl_3$-KCl					
0.0	100.0	2.011	−0.609	849—1000	0.123
15.2	84.8	2.377	−0.615	820—1005	0.205
28.4	71.6	2.662	−0.640	832—1010	0.304
42.4	57.6	3.048	−0.738	810—1010	0.695
59.3	40.7	3.433	−0.828	748—1008	1.13
69.7	30.3	3.638	−0.885	772—1010	1.21
86.2	13.8	3.850	−0.875	724—1004	0.821
(e) $NdCl_3$-NaCl					
0.0	100.0	2.024	−0.573	838—1021	0.375
12.5	87.5	2.376	−0.537	858—1011	6.88
26.2	73.8	2.843	−0.692	820—1010	1.03
39.3	60.7	3.154	−0.720	743—1010	0.336
55.3	44.7	3.489	−0.783	750—1009	0.581
68.5	31.5	3.696	−0.857	732—1008	1.94
85.0	15.0	3.890	−0.843	748—1000	0.500
(f) $NdCl_3$-$CaCl_2$					
0.0	100.0	2.473	−0.424	825—1011	0.504
14.4	85.6	2.684	−0.442	820—1003	0.590
27.2	72.8	3.054	−0.623	730—1010	1.12
45.4	54.5	3.356	−0.688	730—1024	1.21
60.8	39.2	3.560	−0.701	733—1009	1.42
74.5	25.5	3.760	−0.794	730—1011	2.28
84.5	15.5	3.837	−0.737	740—1018	0.813

TABLE 3. MOLAR VOLUME ISOTHERM EQUATIONS OF BINARY MIXTURE SYSTEMS IN MOLTEN STATE

Binary system	Temp. (°C)	$V_{mix}=A+BX$ (V_{mix}: cm³/mol, X: mole fraction)	σ (cm³/mol)
$PrCl_3$-KCl	800	$V_{mix}=50.5+25.3X$	1.71
	1000	$V_{mix}=54.2+26.4X$	1.46
$PrCl_3$-NaCl	800	$V_{mix}=37.2+37.7X$	1.07
	1000	$V_{mix}=39.8+39.3X$	1.17
$PrCl_3$-$CaCl_2$	800	$V_{mix}=52.3+21.5X$	1.09
	1000	$V_{mix}=54.4+24.0X$	1.56
$NdCl_3$-KCl	800	$V_{mix}=49.8+25.4X$	0.98
	1000	$V_{mix}=53.7+25.5X$	0.80
$NdCl_3$-NaCl	800	$V_{mix}=37.5+37.2X$	0.51
	1000	$V_{mix}=40.2+38.4X$	0.59
$NdCl_3$-$CaCl_2$	800	$V_{mix}=52.3+22.0X$	0.81
	1000	$V_{mix}=54.6+23.6X$	0.84

X: mole fraction of rare-earth chloride in mixture melt

indicate the simple eutectic melts, and have no intermediate compounds. The linear molar volume isotherms of these systems at 800 and 1000 °C are the reasonable results, which may suggest the random mixing of ions in molten state. But the phase diagrams of $PrCl_3$–KCl[3,5] and $NdCl_3$–KCl[5] systems show the formation of intermediate compounds, and though the existance of complex ions in these mixture melts might be expected, the molar volume isotherms at 800 and 1000 °C have the linear behaviors.

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