Surface Tensions of Molten Binary $PrCl_3$-NaCl, $PrCl_3$-KCl, and $PrCl_3$-$CaCl_2$ Systems

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Synopsis. The surface tensions of molten binary $PrCl_3$-NaCl, $PrCl_3$-KCl, and $PrCl_3$-$CaCl_2$ systems were measured by a maximum bubble pressure method, and the results were expressed as linear functions of the temperature. The isotherms of surface tension of the $PrCl_3$-MCl (M=Na and K) systems had minimum; however, such behavior was not observed in the isotherm of the $PrCl_3$-$CaCl_2$ system.

An investigation of the surface tension of molten salts is of interest in understanding the characteristics of the melts. The surface tensions of some molten binary RCl_3-MCl (M=alkali metal) mixtures containing rare earth chlorides RCl_3 have been measured by Smirnov and Stepanov,[1] Kurmaev et al.,[2] and Igarashi et al.,[3] but those of molten binary systems containing $PrCl_3$ have not yet been reported. We have already measured the densities,[4] refractive indexes,[5] and electrical conductivities[6] of molten $PrCl_3$-alkali and -alkaline earth chloride mixtures in order to elucidate the physical properties of charge-asymmetric melts. In the present study the surface tensions of molten binary $PrCl_3$-NaCl, $PrCl_3$-KCl, and $PrCl_3$-$CaCl_2$ mixtures were measured.

Experimental

Chemicals. $PrCl_3$ was prepared and purified in the same way as that previously reported.[5] Impurities in the purified $PrCl_3$ were analyzed, their contents being less than 100 ppm.[6] The chemicals NaCl, KCl, and $CaCl_2$ were of analytical reagent grade, and dried with conventional techniques.[7] The prepared mole ratios of mixtures were checked by chelate titration.

Measurement Procedure. In the present study the maximum bubble pressure method was applied for determining the surface tension of melts because of the precision of the measurement at the elevated temperature. As working gas argon was used, which was purified by passing through chemical traps filled with molecular sieves 4A and titanium sponges at 900 °C to remove possible H_2O, N_2, and O_2 contaminations. A manometer filled with *n*-butyl phthalate colored red by a dyestuff was used to measure the pressure of the working gas bubble, which was kept at 30.4±0.1 °C by a circulation of thermostatted water. The temperature of a furnace was raised above the liquidus temperature of the sample according to the phase diagrams[8,9] and kept constant. The temperature of the melts was maintained within ±1 °C with a temperature controller, and measured with a C.A. thermocouple sheathed with a fused silica tube. Pt-10%Rh alloy capillary was used for a creation of bubble. The accurate inside diameter of the capillary tip was determined by the surface tension of distilled water at room temperature. The diameter of the capillary at elevated temperature was corrected by use of the coefficient of thermal expansion for the alloy.[10] The surface tensions of the melts were calculated using Schrödinger's equation[11] giving the relation between bubble pressure and surface tension.

Results and Discussion

The surface tensions of molten pure NaCl, KCl, and $CaCl_2$ obtained were compared with the values recommended by Janz et al.[12,13] Our results yield smaller values than the recommended ones, but the departures are within 1%. There are no data on the surface tension of molten $PrCl_3$ except our data.[3]

The surface tensions of these binary systems in the liquid state were represented as linear functions of temperature, $\gamma=a-bt$, (t/°C). The parameters a and b obtained by the method of least squares are summarized in Table 1. The isotherms of surface tension for the molten $PrCl_3$-NaCl, $PrCl_3$-KCl, and $PrCl_3$-$CaCl_2$ systems at 850, 900, and 950 °C are shown in Figs. 1, 2, and 3, respectively. The isotherm at each temperature of the $PrCl_3$-NaCl system had a minimum at about 60 mol% $PrCl_3$. The minimum was also observed in the isotherm of the $PrCl_3$-KCl system, but the composition in the minimum was recognized to shift to low concentration of $PrCl_3$, i.e., about 30 mol% $PrCl_3$. On the other hand, as can be seen in Fig. 3, the isotherms of the $PrCl_3$-$CaCl_2$ system showed quite different behavior, i.e., the surface tension decreased curvilinearly with a increase of

Table 1. Surface Tensions of Molten Binary $PrCl_3$-NaCl, $PrCl_3$-KCl, and $PrCl_3$-$CaCl_2$ Systems

	$\gamma=a-bt$	$\gamma/10^{-3}$ N m^{-1}, t/°C			
System	$PrCl_3$ mol%	a	$b\times10^{-2}$	σ	Temp range/°C
$PrCl_3$-NaCl	0.0	173.07	7.47	0.18	830—950
	29.0	149.35	5.58	0.23	820—929
	43.1	164.29	7.47	0.06	890—930
	57.1	151.79	6.25	0.19	878—940
	71.0	153.90	6.40	0.11	815—925
	86.2	158.90	6.74	0.09	875—910
	100.0	135.96	3.73	0.03	830—926
$PrCl_3$-KCl	0.0	157.07	7.52	0.23	854—936
	20.0	147.93	6.69	0.27	818—939
	43.1	139.77	5.59	0.26	820—940
	57.1	134.59	4.82	0.10	842—942
	70.9	131.22	4.04	0.10	820—949
	86.0	130.67	3.70	0.19	881—952
$PrCl_3$-$CaCl_2$	0.0	178.18	3.95	0.29	800—946
	20.0	193.58	6.99	0.23	880—930
	29.9	171.07	5.21	0.24	850—940
	43.0	180.39	6.63	0.08	865—930
	55.6	163.41	5.55	0.22	870—940
	71.0	141.94	3.94	0.33	870—940
	86.0	138.03	3.87	0.10	840—940

σ is the standard error of estimate in 10^{-3} N m^{-1}.

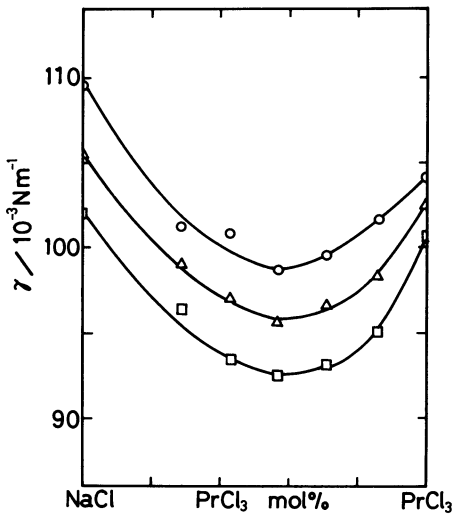

Fig. 1. Isotherms of surface tension of molten $PrCl_3$–NaCl system at 850(○), 900(△), and 950(□)°C.

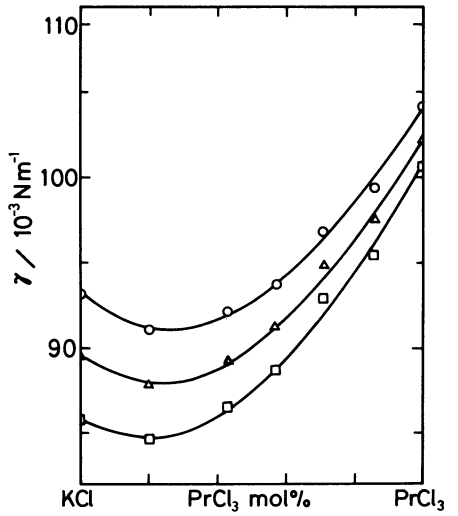

Fig. 2. Isotherms of surface tension of molten $PrCl_3$–KCl system at 850(○), 900(△), and 950(□)°C.

$PrCl_3$ concentration without the minimum. We have measured the surface tensions of molten $LaCl_3$–MCl (M=Na[14] and K[15]) and -$CaCl_2$[14] systems. A similar behavior to the isotherms of surface tension of the $PrCl_3$ systems observed in this work has also been found in the corresponding three $LaCl_3$ mixtures. There are no data available on the structure of molten chloride mixtures containing $PrCl_3$. Fortunately, the structure of molten $LaCl_3$–MCl(M=Na[16] and K[16–18]) and -$CaCl_2$[16] systems has been investigated by Raman spectroscopy. The ionic radius of Pr^{3+} ion is 0.099 nm, which is almost equal to that of La^{3+} ion, viz., 0.1032 nm.[19] From the similarity of the density in valence and the very small difference in ionic radii, 0.004 nm, the structures of the molten $PrCl_3$ systems are expected to be extremely close to those of the corresponding molten $LaCl_3$ systems. In the alkali chloride-rich $PrCl_3$–NaCl and $PrCl_3$–KCl melts, a $PrCl_6^{3-}$ octahedron is thought to be a predominant

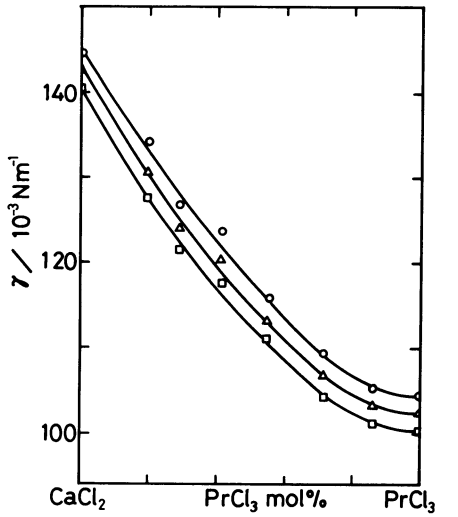

Fig. 3. Isotherms of surface tension of molten $PrCl_3$–$CaCl_2$ system at 850(○), 900(△), and 950(□)°C.

configuration since a similar species is found in the alkali chloride-rich $LaCl_3$–NaCl and $LaCl_3$–KCl melts.[16–18] The complex behavior of the isotherms of the surface tension in both systems seems to be due to such complex species formed in the melts. It has been reported that there exists little such octahedral complex species in the $LaCl_3$–$CaCl_2$ system.[16] The fact implies that the $PrCl_3$–$CaCl_2$ system does not deviate significantly from a cation random mixture. A simple composition change of the surface tension in this system seems to be attributable to such mixing of the melt.

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