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Surface Tensions of Several Rare-earth Chlorides and Binary NaCl–YCl_3 System in Molten State

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Synopsis. The surface tensions of YCl_3, $LaCl_3$, $PrCl_3$, $NdCl_3$, $GdCl_3$, and $DyCl_3$, and binary NaCl-YCl_3 system in molten state were measured by a maximum bubble pressure method, and the results were represented by empirical formulas as functions of temperature. Surface enthalpies of rare-earth chlorides were calculated from the formulas.

Surface tension is important for thermodynamic considerations, since it is related to the interaction between the species in the melts and is necessary for calculating surface properties such as surface enthalpy and surface entropy. The surface tensions of binary $LaCl_3$–alkali chloride and –alkaline earth chloride systems in molten state have been reported by Smirnov and Stepanov¹⁾ and those of binary $NdCl_3$–alkali chloride systems in molten state by Kurmaev *et al.*²⁾ In the present experiment, the surface tensions of YCl_3, $LaCl_3$, $PrCl_3$, $NdCl_3$, $GdCl_3$, and $DyCl_3$, and binary NaCl–YCl_3 system were measured, and represented by empirical formulas as functions of temperature. Negative deviation from the surface tension calculated by use of Guggenheim's equation³⁾ for ideal solution takes place in the isotherm of surface tension for binary NaCl–YCl_3 system.

Experimental

Materials. Rare-earth chlorides were prepared by the similar procedure to that given in the previous paper.⁴⁾ NaCl of analytical grade was dried by heating *in vacuo* at temperature 50 °C below the melting point for several hours. Argon gas was purified by passing through P_2O_5 and heated Ti sponges at 1000 °C.

Measurement. Maximum bubble pressure method was used. Two types of capillaries were used, one made of transparent quartz and the other of Pt-Rh(10% Rh) alloy. The surface tensions of binary NaCl-YCl_3 mixture melts were measured with the quartz capillary. The pressure of argon bubbles in the melts was measured with a manometer containing dibutyl phthalate, which was kept at 30.4±0.1 °C in a water bath. The surface tensions were calculated by means of Schrödinger's⁵⁾ equation giving the relation between bubble pressure and surface tension. The surface tension of NaCl and $CaCl_2$ in molten state were measured to check the apparatus, the observed values being in good agreement with the data given by Bloom *et al.*⁶⁾ and Grjotheim *et al.*⁷⁾

Results and Discussion

Surface Tensions of Rare-earth Chlorides. The temperature dependence of the surface tensions for YCl_3, $LaCl_3$, $PrCl_3$, $NdCl_3$, $GdCl_3$, and $DyCl_3$ in molten state are shown in Fig. 1. The surface tension decreases linearly with increasing temperatrue within the range of measurement. The values are represented by linear empirical formulas as functions of temperature. The formulas are given in Table 1, together with standard error, σ.

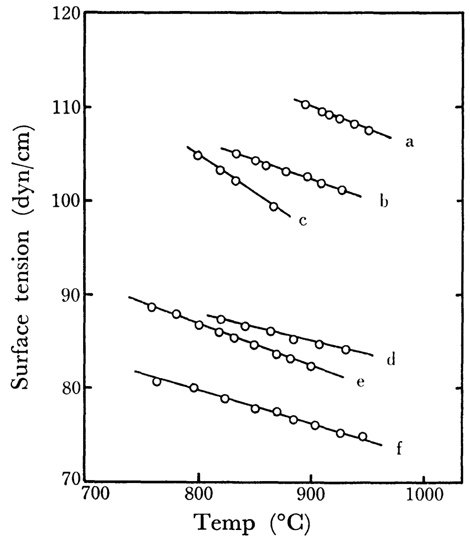

Fig. 1. Surface tensions of rare-earth chloride melts. a: $LaCl_3$, b: $PrCl_3$, c: $NdCl_3$, d: $GdCl_3$, e: $DyCl_3$, f: YCl_3.

TABLE 1. SURFACE TENSION EQUATIONS OF PURE MOLTEN SALTS

Salt	$\gamma=a+bt$ γ : (dyn/cm), t(°C)	σ (dyn/cm)	Temp range (°C)
YCl_3	$\gamma=106.3-0.0334t$	0.158	768—946
$LaCl_3$	$\gamma=147.9-0.0423t$	0.121	892—950
$PrCl_3$	$\gamma=135.9-0.0372t$	0.034	830—926
$NdCl_3$	$\gamma=173.4-0.0855t$	0.166	800—865
$GdCl_3$	$\gamma=110.1-0.0278t$	0.139	820—930
$DyCl_3$	$\gamma=124.4-0.0465t$	0.069	760—901

The values obtained for $LaCl_3$ melts were slightly lower than that reported by Smirnov *et al.*⁸⁾

Surface Enthalpies of Rare-earth Chlorides. The surface enthalpies of rare-earth chlorides in molten state were calculated by the equation

$$H^s = \gamma - T\left(\frac{d\gamma}{dT}\right),$$

where H^s is the surface enthalpy in erg/cm², γ the surface tension of molten salt in dyn/cm, and T the absolute temperature. The results are given in Table 2. Comparing the surface enthalpies of the molten chlorides with those of other molten salts, we see that the molten chlorides have similar surface enthalpies except for YCl_3, $NdCl_3$, and $GdCl_3$ melts. The values of

Table 2. Surface enthalpies of pure molten salts

Salt	H^s (erg/cm^2)
YCl_3	115.4
$LaCl_3$	159.5
$PrCl_3$	146.1
$NdCl_3$	196.8
$GdCl_3$	117.7
$DyCl_3$	137.1

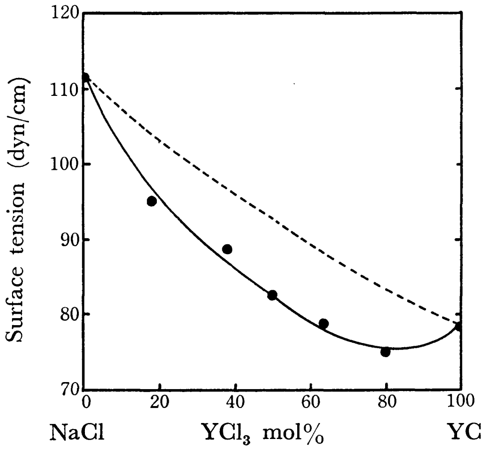

Fig. 2. Isotherm of surface tension of molten binary NaCl-YCl_3 mixture at 825 °C.
—●—: Observed surface tensions, ----: calculated surface tensions by use of the Guggenheim's equation for ideal solution.

Table 3. Surface tension equations of molten binary NaCl-YCl_3 system

YCl_3 (mol%)	$\gamma = a + bt$ γ : (dyn/cm), t(°C)	σ (dyn/cm)	Temp range (°C)
0.0	$\gamma = 173.1 - 0.0747\,t$	0.180	830—950
17.7	$\gamma = 165.2 - 0.0853\,t$	0.332	819—910
38.1	$\gamma = 140.2 - 0.0628\,t$	0.420	747—901
50.0	$\gamma = 111.8 - 0.0346\,t$	0.113	787—857
63.8	$\gamma = 108.0 - 0.0350\,t$	0.136	795—938
80.0	$\gamma = 94.9 - 0.0239\,t$	0.166	806—876
100.0	$\gamma = 106.3 - 0.0334\,t$	0.158	768—946

the molten YCl_3 and $GdCl_3$ were intermediate between those of the molten chlorides and covalent liquids such as benzene and methanol, the value of $NdCl_3$ being larger than that of the others.

Binary NaCl–YCl_3 Mixture. The isotherm of surface tension of molten binary NaCl–YCl_3 mixture at 825 °C is shown in Fig. 2. The surface tensions are represented by empirical formulas as functions of temperature. The results are given in Table 3. In binary molten salt mixtrures with a common anion, the surface tensions show a negative deviation from surface tension isotherms of ideal solution calculated by use of Guggenheim's equation. In this binary NaCl–YCl_3 mixture, a large negative deviation was observed. The negative deviation at 825 °C is shown in Fig. 3.

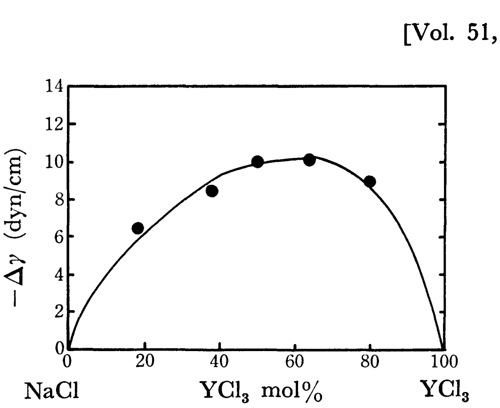

Fig. 3. Negative deviation of molten binary NaCl-YCl_3 mixture at 825 °C.

The maximum value of the deviation was observed at about 65 mol% in YCl_3. For the calculations of surface tensions, the densities of these melts were used with the data given in previous papers.[9–11]

The calculations were carried out with the computer at Chiba University.

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