Surface Tensions of Molten Binary $\text{CaCl}_2\text{-NaCl}$, $\text{LaCl}_3\text{-NaCl}$, and $\text{LaCl}_3\text{-CaCl}_2$ and Ternary $\text{LaCl}_3\text{-CaCl}_2\text{-NaCl}$ Systems

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The surface tensions of the molten binaries $\text{CaCl}_2\text{-NaCl}$, $\text{LaCl}_3\text{-NaCl}$, and $\text{LaCl}_3\text{-CaCl}_2$ and the three quasi-binaries $\text{LaCl}_3\text{-}n\text{NaCl}\cdot m\text{CaCl}_2$ (mole ratios $n:m = 2.7:1$, $1:1$, and $1:3.1$) were measured by the maximum bubble pressure method. The surface tension of $\text{CaCl}_2\text{-NaCl}$ and $\text{LaCl}_3\text{-CaCl}_2$ increases curvilinearly with increasing CaCl_2 concentration, while below 900°C the isotherms of $\text{LaCl}_3\text{-NaCl}$ show a minimum at ca. 30 mol% LaCl_3 . A minimum was also observed for the quasi-binary with $n:m = 2.7:1$. The surface tensions for the ternary $\text{LaCl}_3\text{-CaCl}_2\text{-NaCl}$ at 900°C were constructed from the above results.

Introduction

Molten binary and ternary mixtures of LaCl_3 , CaCl_2 , and NaCl are interesting because the cations La^{3+} (1.045 Å), Ca^{2+} (1.00 Å), and Na^+ (1.02 Å) have different charge but nearly equal ionic radii [1]. In a previous study on molten $\text{CaCl}_2\text{-NaCl}$, $\text{LaCl}_3\text{-NaCl}$, $\text{LaCl}_3\text{-CaCl}_2$ and $\text{LaCl}_3\text{-CaCl}_2\text{-NaCl}$ [2] it was found that the molar volumes of molten $\text{LaCl}_3\text{-NaCl}$ and $\text{LaCl}_3\text{-CaCl}_2$ show positive and negative deviations from additivity, respectively, while those of $\text{CaCl}_2\text{-NaCl}$ and the quasi-binary $\text{LaCl}_3\text{-}n\text{NaCl}\cdot m\text{CaCl}_2$ ($n:m$ = mole ratio) are approximately additive. It is of much interest to see if these bulk property are reflected in the surface tension.

There exist some data on the surface tension of molten $\text{CaCl}_2\text{-NaCl}$ [3] but none on $\text{LaCl}_3\text{-NaCl}$, $\text{LaCl}_3\text{-CaCl}_2$ and the ternary mixtures. The surface tension of $\text{LaCl}_3\text{-KCl}$ has been measured in [4].

In the present study the surface tensions of the molten binaries $\text{CaCl}_2\text{-NaCl}$, $\text{LaCl}_3\text{-NaCl}$, and $\text{LaCl}_3\text{-CaCl}_2$, and the quasi-binaries $\text{LaCl}_3\text{-}n\text{NaCl}\cdot m\text{CaCl}_2$ (mole ratios $n:m = 2.7:1$, $1:1$, and $1:3.1$) were measured and discussed.

Experimental

Chemicals and Melt Preparation

LaCl_3 was prepared and purified in the same way as reported in [5]. Impurities in the purified LaCl_3

crystal were determined by emission spectroscopy, the result being almost the same as reported in [2]. The chemicals NaCl and CaCl_2 were of analytical reagent grade. They were dried under vacuum of 10^{-3} Torr by heating 50°C below their melting points for 8 hours and then melted. All the chemicals were stored in ampoules after solidification. The prepared mole ratios of the mixtures were checked by chelate titration.

Method and Procedure

As in [4], the maximum bubble pressure method was applied because of the precision of this method at high temperatures. 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 . The manometer filled with di-*n*-butyl phthalate containing a red color dyestuff was kept at $30.4 \pm 0.1^\circ\text{C}$ by thermostated water. After filling the sample cell with the working gas, its temperature was raised above the liquidus temperature as taken from a phase diagram [6, 7] and maintained within $\pm 1^\circ\text{C}$ with a temperature controlling device. The temperature of the melt was measured with a C.A. thermocouple sheathed with a fused silica tube.

A Pt-10% Rh alloy capillary was used for the creation of the bubble. The inside diameter of the capillary tip was determined by a measurement of the surface tension of distilled water at room temperature. For the elevated temperatures the diameter

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was corrected with the coefficient of thermal expansion of the alloy [8]. Details of the method are described in [4].

The surface tension, γ , was calculated by the equation

$$\gamma = r g (h d_1 - i d_2) / 2 - d_2 r^2 g / 3 - d_2^2 r^3 g / [12 (h d_1 - i d_2)], \quad (1)$$

where $2r$ is the inside diameter of the capillary, g the acceleration of gravity, h the height of manometer column, d_1 the density of di-n-butyl phthalate, d_2 the density of the melt, which was obtained from the molar volume data [2], i the depth of the immersion of the capillary into the melt.

Results and Discussion

Pure Melts

As in [5], the surface tension of molten LaCl_3 could be expressed as

$$\gamma = 147.90 - 0.0423 t, \quad t / ^\circ\text{C}.$$

Figure 1 shows the surface tensions reported in the literature with those obtained in this work for molten NaCl and CaCl_2 . The values for molten CaCl_2 and NaCl recommended by Janz *et al.* [3, 13] are based on [11]. Our results yield smaller values, but the departures are within 1%.

Binary Melts

The surface tensions of the binary mixtures were expressed as linear functions of temperature by means of a least squares regression. The results listed in Table 1, in which δ is the standard error of estimate in dyn cm^{-1} .

Two surface tension isotherms of molten CaCl_2 -NaCl are shown in Fig. 2 together with that reported by Grjotheim *et al.* [11]. The agreement with [11] is excellent. The surface tensions of this system increased curvilinearly with the increase of CaCl_2 concentration in both temperatures. The tendency is in good agreement with the reported one. Similar tendency was also found in a composition dependence of surface tension for the molten LaCl_3 - CaCl_2 system as shown in Figure 4. On the other hand, as

Fig. 1. Comparison of surface tensions reported in the literature with those obtained in this work. [A] NaCl ($-\circ-$), [B] CaCl_2 ($-\square-$), a [9], b [10], c [11], d [12], e [13], f [14], g [15].

Fig. 2. Surface tension isotherms of molten CaCl_2 -NaCl at 800 (Δ) and 900 ($\circ$) $^\circ\text{C}$. — Symbol $\bullet$ denotes the data of Grjotheim *et al.* [11].

can be seen in Fig. 3, the isotherms of the molten LaCl_3 -NaCl system differ evidently from those of the former two systems. That is, the isotherms at temperature below 900 $^\circ\text{C}$ have a minimum at ca. 30 mol% LaCl_3 . Such a behavior is similar to that found in the composition dependence of surface tension for the molten LaCl_3 -KCl system [5].

Recently, it has been found by Raman spectroscopy [16] that LaCl_6^{3-} exists in NaCl-rich LaCl_3 -NaCl and in LaCl_3 -KCl [17, 18] but little of that

Table 1. Surface tensions of the molten binaries CaCl_2 -NaCl, LaCl_3 -NaCl and LaCl_3 - CaCl_2 . δ is the standard error of estimate.

$\gamma = a - bT$		$\gamma/\text{dyn cm}^{-1}, T/^{\circ}\text{C}$		
mol%	a	$b \times 10^{-2}$	$\delta/\text{dyn cm}^{-1}$	Temp. range/ $^{\circ}\text{C}$
(a) CaCl_2 -NaCl (CaCl_2 mol%)				
0.0	173.08	7.47	0.18	830 – 950
10.0	175.48	7.56	0.06	838 – 950
20.6	174.59	6.99	0.21	830 – 940
40.1	163.06	4.93	0.26	809 – 926
50.0	164.66	4.73	0.19	824 – 945
61.4	166.40	4.69	0.32	794 – 930
90.0	179.96	4.54	0.39	811 – 950
100.0	180.84	4.23	0.23	823 – 946
(b) LaCl_3 -NaCl (LaCl_3 mol%)				
10.0	160.04	5.97	0.13	815 – 933
35.1	145.37	4.39	0.21	820 – 936
50.0	149.92	4.84	0.13	853 – 940
74.8	152.53	4.84	0.05	840 – 891
90.0	148.90	4.39	0.13	874 – 945
(c) LaCl_3 - CaCl_2 (LaCl_3 mol%)				
17.0	177.32	5.02	0.08	885 – 940
32.9	178.78	5.88	0.12	855 – 939
50.1	171.16	5.65	0.20	874 – 938
67.1	160.95	5.26	0.12	886 – 940
83.0	155.23	4.91	0.11	908 – 950

Fig. 3. Surface tension isotherms of molten LaCl_3 -NaCl at 850 (Δ), 900 ($\circ$), and 950 ($\square$) $^{\circ}\text{C}$.

species in LaCl_3 - CaCl_2 . The structure of molten CaCl_2 -NaCl has been investigated by X-ray diffraction [19]: a calcium ion in the melt is claimed to be surrounded by about six chloride ions; the existence of this octahedral complex is however not yet confirmed. Therefore, the surface tension of molten

Fig. 4. Surface tension isotherms of molten LaCl_3 - CaCl_2 at 850 (Δ), 900 ($\circ$), and 950 ($\square$) $^{\circ}\text{C}$.

LaCl_3 -NaCl seems to be affected by the LaCl_6^{3-} octahedron formed in the NaCl-rich melt. This is analogous to the behavior found in the surface tension of molten MgCl_2 -KCl [11, 20], in which the existence of tetrahedral species MgCl_4^{2-} has been confirmed by Raman spectroscopy [21, 22].

The surface energy of mixing per unit area, $\Delta E^s/a$, is given by [14]

$$\Delta E^s/a = E^s/a - [X_1(E^s/a)_1 + X_2(E^s/a)_2],$$

where X_1 and X_2 are the mole fractions of the components 1 and 2, respectively, and E^s/a and $(E^s/a)_i$ ($i=1, 2$) are the surface energies per unit area of the mixture and the constituent pure melts, respectively. They are related to the surface tension by the equations

$$E^s/a = \gamma - T(d\gamma/dT),$$

$$E_i^s/a = \gamma_i - T(d\gamma_i/dT),$$

where T is the absolute temperature. The surface energy of mixing of a molten mixture is one of the useful surface properties [20]. The calculated results for the binary systems are given in Fig. 5 together with the composition dependence of the excess molar volumes obtained in [2]. Evidently, these show an opposite composition dependence. $\Delta E^s/a$ of LaCl_3 -NaCl, with its positive excess molar volume, its maximum being at 30 mole% LaCl_3 , has a large negative value at the same concentration. This is similar to $\Delta E^s/a$ of LaCl_3 -KCl [5], denoted by the dashed line. Small negative values are

Fig. 5. Composition dependence of surface energies of mixing per unit area and excess molar volumes at 900 °C. — 1: LaCl_3 -NaCl, 2: LaCl_3 - CaCl_2 , and 3: CaCl_2 -NaCl. $\Delta E^s/a$ of molten LaCl_3 -KCl [4] is also shown (dashed line).

Fig. 6. Surface tension isotherms of molten quasi-binary systems at 900 °C. — (---) LaCl_3 -NaCl, (○) LaCl_3 - $n\text{NaCl}.m\text{CaCl}_2$ ($n:m = 2.7:1$), (□) LaCl_3 - $n\text{NaCl}.m\text{CaCl}_2$ (1:1), (Δ) LaCl_3 - $n\text{NaCl}.m\text{CaCl}_2$ (1:3.1), and (----) LaCl_3 - CaCl_2 .

observed for CaCl_2 -NaCl, whose molar volume is additive. On the contrary, the $\Delta E^s/a$ of LaCl_3 - CaCl_2 with its negative excess molar volume has small positive values over the whole composition range. These results show that the surface energy of mixing of molten salt mixtures is correlated with the characteristics of the melt and the excess molar volume.

Fig. 7. Surface tension isotherms of the molten ternary LaCl_3 - CaCl_2 -NaCl system at 900 °C (unit: dyn cm^{-1}). — Dashed lines a, b, and c indicate the quasi-binary systems measured and dotted lines denote somewhat uncertain isotherms.

Table 2. Surface tensions of molten quasi-binary systems.

$\gamma = a - b t$		$\gamma/\text{dyn cm}^{-1}, t/^{\circ}\text{C}$		
mol%	a	$b \times 10^{-2}$		Temp. range/ $^{\circ}\text{C}$
(a) $\text{LaCl}_3\text{-}n\text{NaCl}.m\text{CaCl}_2$ ($n:m = 2.7:1$)				
16.8	169.69	6.38	0.19	865 – 970
30.4	150.19	4.55	0.30	882 – 955
45.1	145.04	4.20	0.30	903 – 981
59.5	148.13	4.47	0.19	870 – 975
73.1	145.90	4.18	0.08	873 – 920
(b) $\text{LaCl}_3\text{-}n\text{NaCl}.m\text{CaCl}_2$ ($n:m = 1:1$)				
10.3	155.62	3.92	0.30	811 – 946
18.8	154.52	4.00	0.13	823 – 954
35.0	152.01	3.99	0.37	842 – 934
50.0	148.93	3.83	0.45	838 – 937
70.8	145.82	3.69	0.19	851 – 950
85.5	141.26	3.29	0.14	868 – 962
(c) $\text{LaCl}_3\text{-}n\text{NaCl}.m\text{CaCl}_2$ ($n:m = 1:3.1$)				
10.2	176.09	5.27	0.34	879 – 950
30.2	172.02	5.58	0.14	840 – 972
46.0	161.02	4.67	0.15	838 – 960
59.7	145.47	3.27	0.21	836 – 951
74.5	143.09	3.16	0.19	850 – 972
89.3	144.74	3.62	0.24	865 – 962

Ternary Melts

The surface tensions of the molten ternary LaCl_3 - CaCl_2 -NaCl were measured for varying LaCl_3 content at constant mole ratio $\text{CaCl}_2/\text{NaCl}$, i.e. for the three quasi-binary systems LaCl_3 -

$n\text{NaCl} \cdot m\text{CaCl}_2$ with $n:m = 2.7:1$ (a), $n:m = 1:1$ (b) and $n:m = 1:3.1$ (c). The surface tensions obtained were also represented as linear functions of temperature. The parameters determined by the least squares fit are listed in Table 2. Figure 6 shows the composition dependence of the surface tension of these mixtures at 900°C . In the LaCl_3 - $n\text{NaCl} \cdot m\text{CaCl}_2$ ($2.7:1$) system with the low concentration of CaCl_2 , the isotherm has a minimum similar to that of the binary LaCl_3 -NaCl. But this

tendency disappears with increase of the concentration of CaCl_2 . This appears to be due to an inhibition of the formation of LaCl_6^{3-} by the presence of CaCl_2 .

Figure 7 shows roughly the isotherms of surface tension of the LaCl_3 - CaCl_2 -NaCl at 900°C according to the isotherms of the three binaries and the three quasi-binaries. The dashed lines a, b, and c indicate the quasi-binary systems measured.

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