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

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The surface tensions of the molten binaries CaCl$_2$-NaCl, LaCl$_3$-NaCl, and LaCl$_3$-CaCl$_2$ and the three quasi-binaries LaCl$_3$-nNaCl.mCaCl$_2$ (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 CaCl$_2$-NaCl and LaCl$_3$-CaCl$_2$ increases curvilinearly with increasing CaCl$_2$ concentration, while below 900 °C the isotherms of LaCl$_3$-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 LaCl$_3$-CaCl$_2$-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 CaCl$_2$-NaCl, LaCl$_3$-NaCl, LaCl$_3$-CaCl$_2$ and LaCl$_3$-CaCl$_2$-NaCl [2] it was found that the molar volumes of molten LaCl$_3$-NaCl and LaCl$_3$-CaCl$_2$ show positive and negative deviations from additivity, respectively, while those of CaCl$_2$-NaCl and the quasi-binary LaCl$_3$-nNaCl.mCaCl$_2$ ($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 CaCl$_2$-NaCl [3] but none on LaCl$_3$-NaCl, LaCl$_3$-CaCl$_2$ and the ternary mixtures. The surface tension of LaCl$_3$-KCl has been measured in [4], while those of CaCl$_2$-NaCl and the quasi-binary LaCl$_3$-CaCl$_2$-NaCl are approximately additive. It is of much interest to see if these bulk property are reflected in the surface tension.

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 $10^{-2}$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$_2$, N$_2$, and O$_2$. The manometer filled with di-n-butyl phthalate containing a red color dyestuff was kept at 30.4 ± 0.1 °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 ± 1 °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 was determined by a measurement of the surface tension of distilled water at room temperature. For the elevated temperatures the diameter...
was corrected with the coefficient of thermal expansion of the alloy [8]. Details of the method are described in [4].

The surface tension, \( \gamma \), was calculated by the equation

\[
\gamma = \frac{g (h d_1 - i d_2) / 2 - d_2 r^2 g / 3}{- d_2 i r^2 g / [12 (h d_1 - i d_2)]},
\]

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

\[
\gamma = 147.90 - 0.0423 t, \quad t/\degree C.
\]

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 \( \delta \) 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 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 °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\(_6\)\(^{2-}\) 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$_2$. $\delta$ is the standard error of estimate.

<table>
<thead>
<tr>
<th>mol%</th>
<th>$a$ (CaCl$_2$ mol%)</th>
<th>$b \times 10^{-2}$</th>
<th>$\delta$ (dyn cm$^{-1}$)</th>
<th>Temp. range/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>173.08</td>
<td>7.47</td>
<td>0.18</td>
<td>830 - 950</td>
</tr>
<tr>
<td>10.0</td>
<td>175.48</td>
<td>7.56</td>
<td>0.06</td>
<td>838 - 950</td>
</tr>
<tr>
<td>20.6</td>
<td>174.59</td>
<td>6.99</td>
<td>0.21</td>
<td>830 - 940</td>
</tr>
<tr>
<td>40.1</td>
<td>163.06</td>
<td>4.93</td>
<td>0.26</td>
<td>809 - 926</td>
</tr>
<tr>
<td>50.0</td>
<td>164.66</td>
<td>4.73</td>
<td>0.19</td>
<td>824 - 945</td>
</tr>
<tr>
<td>61.4</td>
<td>166.40</td>
<td>4.69</td>
<td>0.32</td>
<td>794 - 930</td>
</tr>
<tr>
<td>90.0</td>
<td>179.96</td>
<td>4.54</td>
<td>0.39</td>
<td>811 - 950</td>
</tr>
<tr>
<td>100.0</td>
<td>180.84</td>
<td>4.23</td>
<td>0.23</td>
<td>823 - 946</td>
</tr>
<tr>
<td>(b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>160.04</td>
<td>5.97</td>
<td>0.13</td>
<td>815 - 933</td>
</tr>
<tr>
<td>35.1</td>
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<td>4.39</td>
<td>0.21</td>
<td>820 - 936</td>
</tr>
<tr>
<td>50.0</td>
<td>149.92</td>
<td>4.84</td>
<td>0.13</td>
<td>853 - 940</td>
</tr>
<tr>
<td>74.8</td>
<td>132.53</td>
<td>4.84</td>
<td>0.05</td>
<td>840 - 891</td>
</tr>
<tr>
<td>90.0</td>
<td>148.90</td>
<td>4.39</td>
<td>0.13</td>
<td>874 - 945</td>
</tr>
<tr>
<td>(c)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.0</td>
<td>177.32</td>
<td>5.02</td>
<td>0.08</td>
<td>885 - 940</td>
</tr>
<tr>
<td>32.9</td>
<td>178.78</td>
<td>5.88</td>
<td>0.12</td>
<td>855 - 939</td>
</tr>
<tr>
<td>50.1</td>
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<td>5.65</td>
<td>0.20</td>
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</tr>
<tr>
<td>67.1</td>
<td>160.95</td>
<td>5.26</td>
<td>0.12</td>
<td>886 - 940</td>
</tr>
<tr>
<td>83.0</td>
<td>155.23</td>
<td>4.91</td>
<td>0.11</td>
<td>908 - 950</td>
</tr>
</tbody>
</table>

LaCl$_3$-NaCl seems to be affected by the LaCl$_6^-$ 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, $\Delta E^*/a$, is given by [14]

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

where $X_1$ and $X_2$ are the mole fractions of the components 1 and 2, respectively, and $E^{*}/a$ and $(E^{*}/a)_i$ ($i = 1, 2$) 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

$$
E^{*}/a = \gamma - T (d\gamma/dT),
$$

$$
E^{*}/a_i = \gamma_i - T (d\gamma_i/dT),
$$

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. $\Delta E^*/a$ 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 $\Delta E^*/a$ of LaCl$_3$-KCl [5], denoted by the dashed line. Small negative values are
observed for CaCl2-NaCl, whose molar volume is additive. On the contrary, the $\Delta E^*/a$ of LaCl3-CaCl2 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.

**Ternary Melts**

The surface tensions of the molten ternary LaCl3-CaCl2-NaCl were measured for varying LaCl3 content at constant mole ratio CaCl2/NaCl, i.e., for the three quasi-binary systems LaCl3-
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\[ n\text{NaCl} \cdot m\text{CaCl}_2 \text{ with } \frac{n}{m} = 2.7:1 \text{ (a), } \frac{n}{m} = 1:1 \text{ (b) and } \frac{n}{m} = 1:3.1 \text{ (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 LaCl₃-nNaCl.mCaCl₂ (2.7:1) system with the low concentration of CaCl₂, the isotherm has a minimum similar to that of the binary LaCl₃-NaCl. But this tendency disappears with increase of the concentration of CaCl₂. This appears to be due to an inhibition of the formation of LaCl₅⁺ by the presence of CaCl₂.}

Figure 7 shows roughly the isotherms of surface tension of the LaCl₃-CaCl₂-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.