Molar Volume and Surface Tension of Molten $LaCl_3$-KCl Mixtures

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Molar volumes and surface tensions of molten $LaCl_3$-KCl mixtures were measured by dilatometry and the maximum bubble pressure method, respectively. The molar volume isotherms were found to deviate positively from additivity over the whole composition range, with the maximum deviation at ca. 30 mol% $LaCl_3$. At the same concentration the isotherms of surface tension at temperatures below 950 °C show a minimum. Surface energy of mixing per unit area calculated from the surface tensions shows a large negative excess at the corresponding composition. These observations are related to the existence of $LaCl_6^{3-}$ in the KCl-rich melt.

Introduction

Molten $LaCl_3$-KCl is interesting because octahedral $LaCl_6^{3-}$ is reported to exist in the KCl-rich melt [1 – 3]. The density of molten $LaCl_3$-KCl has been measured by Smirnov and Stepanov [4] and by Cho and Kuroda [5]. The molar volume isotherms show positive deviation from additivity. According to [4] the maximum deviation occurs at ca. 70 mol% $LaCl_3$, while according to [5] it occurs at ca. 18 mol% $LaCl_3$. Our own measurements on molten $LaCl_3$-NaCl yielded a maximum at ca. 30 mol% $LaCl_3$ [6]. The surface tension of pure $LaCl_3$ [7] and a few binary melts containing $LaCl_3$ [4, 8] has been measured by Smirnov and Stepanov. Our own measurements on the surface tensions of molten $LaCl_3$ [9] differ considerably as to the temperature dependence.

In this study the molar volume and surface tension of molten $LaCl_3$-KCl mixtures were measured and compared with the reported data [4, 5, 7]. The excess molar volume and surface energy of mixing per unit area were calculated.

Experimental

Chemicals

$LaCl_3$ was synthesized by heating a mixture of La_2O_3 and NH_4Cl. The product was purified by sublimation under reduced pressure. Impurities in the $LaCl_3$ crystal were similar to those reported previously [6]. Analytical reagent grade KCl was dried by heating at a temperature 50 °C below the melting point under vacuum of 10^{-3} Torr for 8 hours. Then the salt was melted and solidified. Chosen amounts of $LaCl_3$ and KCl were weighed in a glove box filled with dry argon. The composition of the molten mixtures was checked by chelate titration.

Measurements

The molar volume of the molten mixtures was measured dilatometrically as described in [6]. For the measurement of the surface tension the maximum bubble pressure method was applied because of its precision at high temperatures. The experimental arrangement is shown in Figure 1. The argon was purified by passing through chemical traps filled with molecular sieves (4 A) and titanium sponges at 900 °C to remove possible H_2O, N_2, and O_2 contaminations. Pressure fluctuations of the gas were buffered by two 5 *l* buffer tanks. The gas flow was adjusted with a needle valve. A fused silica tube was attached to a micrometer screw. A capillary tube of Pt-10% Rh alloy (2 mm outer diameter, 0.2 mm thickness, 80 mm long) sharpend to a knife edge at the tip was attached to the lower end of the silica tube with a graphite joint. A manometer filled with di-n-butyle phthalate coloured red by a dyestuff and kept at 30.4 ± 0.1 °C by thermostated water was used to measure the

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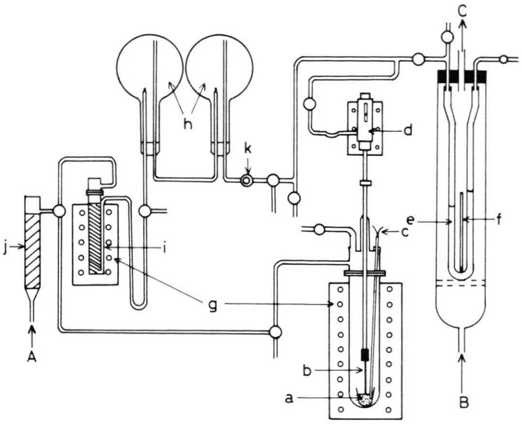

Fig. 1. Schematic diagram of the apparatus for surface tension measurement. a: melt, b: Pt-10% Rh alloy capillary, c: C.A. thermocouple, d: micrometer, e: manometer, f: thermometer, g: electric furnace, h: buffer tank, i: titanium sponge, j: molecular sieves 4A, k: needle valve. A: Ar gas inlet, B: thermostated water inlet, C: thermostated water outlet.

pressure of the working gas bubble. The temperature of the furnace was maintained within ± 1 °C with a controlling device, and the temperature of the sample was measured with a C.A. thermocouple sheathed with a fused silica tube. A fused silica crucible containing the sample was set in the furnace and then the atmosphere in the furnace was exchanged with the working gas. The temperature of the furnace was raised above the liquid temperature of the sample (according to the phase diagram [10]) and kept constant. The capillary was lowered gradually with the micrometer screw while a little working gas was blown from its tip. When the capillary tip got contact with the surface of the melt, a sudden shift of the meniscus in the manometer was observed. The capillary was then inserted to the prescribed depth in the melt by means of the micrometer screw. The meniscus of the manometer liquid was read to 10 μm with a cathetometer.

The inner diameter of the capillary tips was determined by a measurement of the surface tension of distilled water at room temperature, and its diameter at the elevated temperatures was corrected by use of the coefficient of thermal expansion, l_t, for the alloy [11]

$$l_t = l_0 (1 + 9.7 \times 10^{-6}\, t + 8.3 \times 10^{-10}\, t^2), \quad 0 \leqq t/°\mathrm{C} \leqq 1000. \tag{1}$$

The surface tension, γ, of the melt is calculated from

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

where $2r$ is the inside diameter of the capillary, g the acceleration by gravity, h the height of manometer column, d_1 the density of di-n-butyle phthalate, which was measured pycnometrically, d_2 the density of the melt, i the depth of immersion into the melt of the capillary.

Prior to the measurement of the molten sample, the surface tension of molten KNO_3 was measured to know the effect of the immersion depth of the capillary tip on the surface tension. The same surface tension within experimental error was obtained at each immersion depth.

Results and Discussion

Molar Volume

The obtained molar volumes are shown in Figure 2. For molten KCl they agree well with the recomended density data [12], and for molten $LaCl_3$ they are identical to those reported previously [6]. The molar volume obtained for the mixtures can be expressed as

$$V_m\,(\mathrm{cm^3/mol}) = 25.755 + 32.520\,X - 20.540\,X^2 + 19.024\,X^3 + (0.21507 \times 10^{-1} + 0.21770 \times 10^{-2}\,X + 0.25884 \times 10^{-2}\,X^2 - 0.92799 \times 10^{-2}\,X^3)\;T, \tag{3}$$

where T is the temperature in K, X the mole fraction of $LaCl_3$ and the coefficients are least squares fitted to the experimental data. The solid lines in Fig. 2 are obtained from (3). The average percent depature is 0.32%, which is slightly larger than that obtained for other molten binary mixtures containing $LaCl_3$ [6].

Figure 3 shows the molar volume (A) and excess molar volume (B) isotherms at 900 °C. The maximum of the excess molar volume at ca. 30 mol% $LaCl_3$ nearly coincides with that found for the molten $LaCl_3$-NaCl mixtures [6], as shown in Figure 3 (B). Its position does not agree with the results of Smirnov and Stepanov [4] and Cho and Kuroda [5], as mentioned in the Introduction.

Papatheodorou and Østvold [3] have determined the partial enthalpy and partial Gibbs energy of

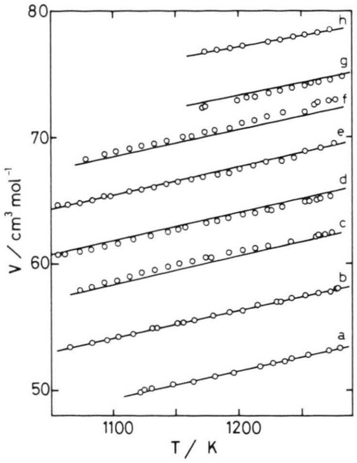

Fig. 2. Molar volume of molten $LaCl_3$-KCl mixtures. Circles indicate the observed values and solid lines those calculated from (3). $LaCl_3$ mol%, a: 0.0, b: 14.2, c: 28.3, d: 42.4, e: 58.2, f: 71.2, g: 84.2, h: 100.0.

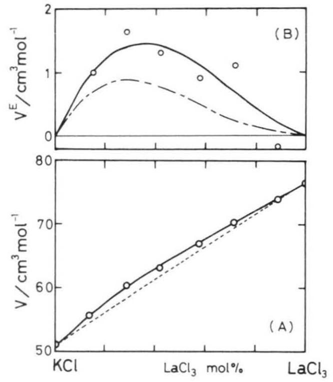

Fig. 3. Molar volume (A) and excess molar volume (B) isotherms of molten $LaCl_3$-KCl at 900 °C. The dashed line in (B) is the excess molar volume of molten $LaCl_3$-NaCl at 900 °C.

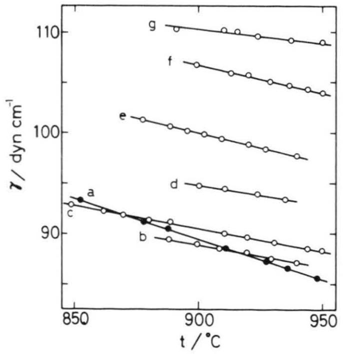

Fig. 4. Surface tension of molten $LaCl_3$-KCl mixtures. $LaCl_3$ mol%, a: 0.0, b: 17.1, c: 33.0, d: 50.0, e: 74.8, f: 87.9, g: 100.0.

Table 1. Surface tension of molten $LaCl_3$-KCl mixtures. σ = standard error of estimate. $\gamma = a - b\,t$ (γ/dyn cm^{-1}, t/°C).

$LaCl_3$ mol%	a	$b \times 10^{-2}$	σ/dyn cm^{-1}	Temp. range/°C
0.0	156.61	7.47	0.21	854–948
17.1	130.01	4.57	0.21	889–940
33.0	130.36	4.43	0.15	849–953
50.0	128.12	3.70	0.14	901–935
74.8	153.55	5.96	0.07	878–940
87.9	157.69	5.66	0.15	899–950
100.0	147.90	4.23	0.12	892–950

mixing of molten $LaCl_3$-KCl mixtures and have indicated tendencies for complex formation in the KCl-rich melt from these thermodynamic data. Furthermore, the existence of the complex $LaCl_6^{3-}$ in the KCl-rich melt has been concluded from Raman spectroscopy by Maroni et al. [1] and Papatheodorou [2]. Due to the strong repulsive interaction of these complexes a maximum of the excess molar volume at 25 mol% $LaCl_3$ would be plausible, which agrees well with our results.

Surface Tension

Figure 4 shows the surface tension of the mixtures vs. temperature and the least squares fitted linear temperature dependences calculated with the coefficients given in Table 1. In Fig. 5 our results on molten KCl are compared with data in the literature [13–16]. The coincidence is good with the exception of the data of Moser et al. [13]. The magnitude of the surface tension of molten $LaCl_3$ is similar to that of molten NaCl [17], and its temperature dependence is similar to that of molten $CaCl_2$ [14]. The surface tension of molten $LaCl_3$ given by Smirnov et al. [7] is

$$\gamma(\text{dyn/cm}) = 272.2 - 0.132\ T/\text{K}.$$

The temperature coefficient of this equation is about twice that reported for alkali and alkaline earth metal chlorides [17, 18]. Also no such large temperature dependences have been found for other rare earth chlorides [9].

As seen in Fig. 4, the addition of $LaCl_3$ to pure KCl changes remarkably the temperature dependence of the surface tension while the change on further addition of $LaCl_3$ is not appreciable. This behaviour corresponds to the minimum at

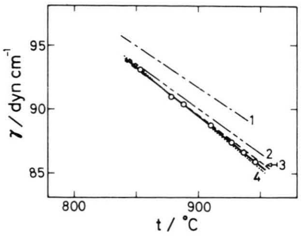

Fig. 5. Comparison of surface tension of molten KCl. 1: [13], 2: [14], 3: [15], 4: [16].

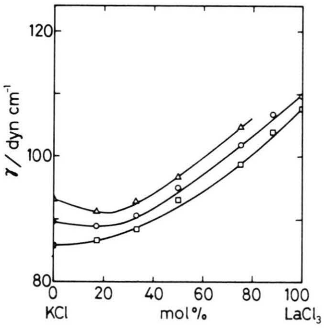

Fig. 6. Surface tension isotherms of molten $LaCl_3$-KCl at 850 (△), 900 (○), and 950 (□) °C.

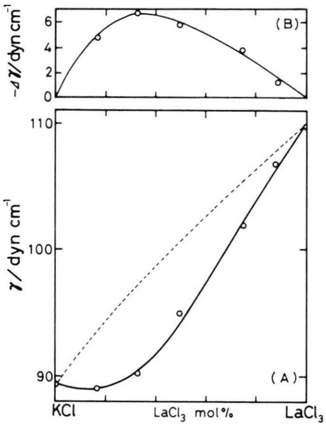

Fig. 7. Surface tension at 900 °C as measured (circles) and as calculated from (4) (A), and difference between the two (B).

ca. 30 mol% $LaCl_3$ in the 850 °C isotherm of Figure 6. The tendency to form minimum was also observed in the isotherms of molten $PrCl_3$-KCl mixtures [19]. In the surface tension measurements on molten $LaCl_3$-KCl mixtures by Smirnov and Stepanov [4] the minimum was not observed.

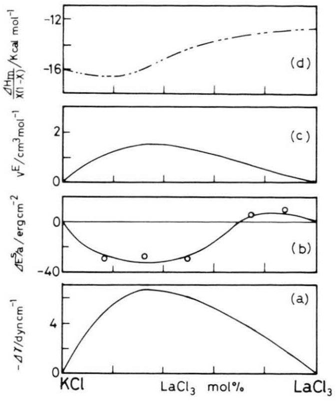

Fig. 8. Composition dependence of surface properties $-\Delta\gamma(a)$ and $\Delta E^s/a$ (b), excess molar volume V^E (c) and heat of mixing (d) [3] for molten $LaCl_3$-KCl mixtures.

Grjotheim et al. [14] have derived a semi-empirical eqation for the surface tension of molten salt mixtures as follows

$$\exp(-\gamma\, a/kT) = \psi_1 \exp(-\gamma_1\, a/kT) + \psi_2 \exp(-\gamma_2\, a/kT), \quad (4)$$

where ψ_i and γ_i are the volume fraction and the surface tension of the i-th component, respectively, and a is the mean area per molecule in the surface layer. ψ_i and a can be given by the equations

$$\psi_i = \bar{V}_i X_i / V_m \quad \text{and} \quad a = (V_m/N)^{2/3}, \quad (5)$$

in which $\bar{V}_i$ and X_i are the partial molar volume and mole fraction of the i-th component, V_m is the molar volume of the melt and N is Avogadro's number. The surface tension at 900 °C was calculated by using (4) and (5) and compared with the observed values in Figure 7(A). Here the partial molar volumes were given by the method of intercepts. It is known that, if complex or complex-like ions are formed in a mixed melt, the observed surface tension deviates largely from that calculated by (4) [16]. As seen in Fig. 7(B), the difference between these values indicates a large maximum at ca. 30 mol% $LaCl_3$.

The surface energy of mixing per unit area is written as follows:

$$\Delta E^s/a = E^s/a - (X(E^s/a)_1 + (1-X)(E^s/a)_2) \quad (6)$$

where E^s/a is the surface energy of the mixture, $(E^s/a)_i$ $(i = 1, 2)$ the surface energy of constituent pure melts, and X the mole fraction. Also

$$E^s/a = \gamma - T(\partial\gamma/\partial T). \tag{7}$$

It is known that in general the surface energy of mixing for ideal molten binary mixtures such as $NaNO_3-NaNO_2$ and $NaNO_3-KNO_3$ becomes near zero, but that in case of complex forming mixtures $\Delta E^s/a < 0$ [16]. The result calculated from (6) is shown in Fig. 8 together with the composition dependence of $-\Delta\gamma$, and V^E obtained in this work and of the heat of mixing reported by Papatheodorou and Østovold [3]. $\Delta E^s/a$ evidently shows a minimum at ca. 30 mol% $LaCl_3$. Small positive values are observed above 70 mol%. These results appear to imply that the formation of complex species such as $LaCl_6^{3-}$ also affects strongly the surface properties of the mixture.

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