Molar Volume 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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Molar volumes of molten $CaCl_2$-NaCl, $LaCl_3$-NaCl, $LaCl_3$-$CaCl_2$ and the quasi-binary systems $LaCl_3$-nNaCl · $m$$CaCl_2$ (mole ratio $n:m$ = 1:3.2, 1:1, and 2.6:1) have been measured by the dilatometric method, and expressed as functions of both temperature and mole fraction by means of least squares regression. The molar volumes of molten $LaCl_3$-NaCl and $LaCl_3$-$CaCl_2$ showed positive and negative deviations, respectively, from additivity, while $CaCl_2$-NaCl and the three quasi-binary systems satisfied approximately the additivity. The isotherm of molar volume for ternary $LaCl_3$-$CaCl_2$-NaCl system at 900 °C was represented according to the isotherms of three binary and three quasi-binary systems.

Introduction

The densities of molten single $LaCl_3$ and $LaCl_3$-MCl (M = alkali metal) mixtures have been measured by Yaffe and van Artsdalen [1], Smirnov and Stepanov [2–4], and Cho and Kuroda [5], and those of molten $LaCl_3$-$BaCl_2$ by Stepanov and Smirnov [6]. However, the densities of molten binary mixtures of $LaCl_3$ with the other alkaline earth chlorides and molten ternary mixtures such as $LaCl_3$-RCl_2-MCl (R = alkaline earth metal) have not yet been measured. Especially the systems $LaCl_3$-$CaCl_2$ and $LaCl_3$-$CaCl_2$-NaCl are interesting because the cations La^{3+} (1.045 Å), Ca^{2+} (1.00 Å), and Na^+ (1.02 Å) have nearly equal ionic radii [7].

The density of molten $CaCl_2$-NaCl has often been measured [8], but there are some differences between the reported data.

In the present paper we report the molar volumes of the molten binaries $CaCl_2$-NaCl, $LaCl_3$-NaCl, and $LaCl_3$-$CaCl_2$ and the quasi-binary $LaCl_3$-nNaCl · $m$$CaCl_2$ (mole ratios $n:m$ = 1:3.2, 1:1, and 2.6:1). These data have been used to determine the molar refractivities [9] and the surface tensions [10] of these melts.

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Experimental

Chemicals and melt preparation

$LaCl_3$ was prepared and purified in the same way as reported in [9]. Impurities in the purified $LaCl_3$ crystal were determined by emission spectrochemical analysis (cf. Table 1). The chemicals NaCl and $CaCl_2$ were of analytical reagent grade. They were dried under vacuume of 10^{-3} Torr by heating 50 °C below their melting point for 8 hours and then melted. All the chemicals were stored in ampoules after solidification. The prepared mole ratios of mixtures were checked by chelate titration.

Method and procedure

Of the different methods for measuring the density of molten salts (maximum bubble pressure method [2–4, 6], pycknometric method [11], dilatometric method [5, 12], Archimedian method [1, 13], manometer method [14]) the dilatometric method has been chosen in view of the hygroscopy of $LaCl_3$ and $CaCl_2$, because in this method the atmosphere is easily controlled.

The furnace assembly is illustrated in Figure 1. The temperature was homogenized by the stainless steel tube inside the quartz tube. The volume of the

Table 1. Impurities in the purified $LaCl_3$ crystal. ±: trace.

Element	Ce	Pr	Ca	Cu	Si	Mg
ppm	30	110	50	±	±	1

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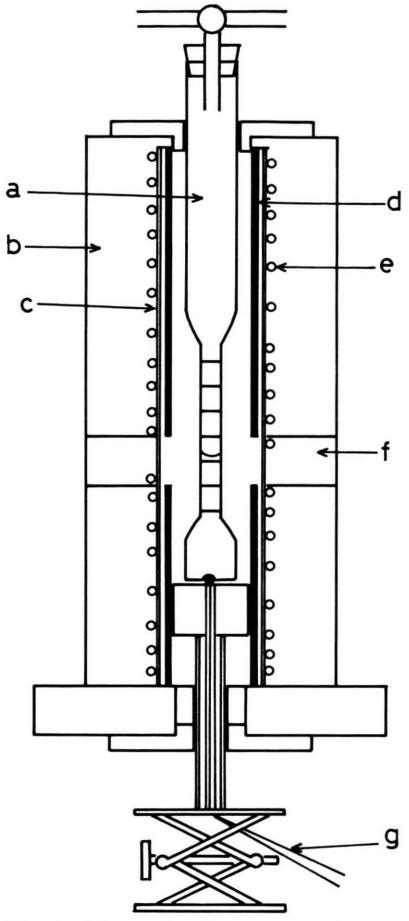

Fig. 1. Schematic diagram of the apparatus for molar volume measurement. a: quartz dilatometer, b: electric furnace, c: quartz tube, d: stainless steel pipe, e: Kanthal wire, f: small window, g: C.A. thermocouple.

quartz dilatometer with its narrow stem was determined with distilled water at room temperature. The volume of the part containing the salt is about 5 cm^3. The error caused by the thermal expansion of the dilatometer in the investigated temperature range was estimated to be less than 0.1%, the thermal expansion coefficient of quartz ($5.5 \times 10^{-7}\ K^{-1}$) [15] being much smaller than that of the molten salts.

The salts were melted under dry argon. The meniscus of the melts was read with a cathetometer. The temperature of the melt was recorded with a precision of ± 0.5 °C with a chromel-alumel thermocouple which is in contact with the bottom of the dilatometer.

Results and Discussion

Pure melts

The density data given in [1], [16], and [17] for molten $LaCl_3$, $CaCl_2$, and NaCl, respectively, have been recommended by Janz et al. [8, 18]. The molar volumes at 900 °C measured in the present work are listed in Table 2 together with those calculated from the recommended data. Our results yield smaller values than the recommended ones, but the departures are within 1%. Similar departures were observed over the measured temperature range for the three pure melts. This means that the dilatometry used in this study is reliable enough to evaluate molar volumes of salts with high melting points as well as low melting points such as alkali metal nitrates [19].

Binary melts

For a representation of the density of molten binary mixtures various polynomial formulas have been used [8, 20]; for the molar volume we have proposed [21] the formula

$$V_m(X, T) = \sum_0^3 a_n X^n + \left(\sum_0^3 b_n X^n\right) T, \qquad (1)$$

where V_m is the molar volume in $cm^3\ mol^{-1}$, X the mole fraction of the cation with the higher valency, and T the absolute temperature. The parameters a_n and b_n as evaluated by a least squares regression of all the data obtained, are listed in Table 3. The average percent departures

$$(\text{a.d.p.}) = \frac{\sum_{i=1}^{N} (100 \times (V_{\text{cal}}^{(i)} - V_{\text{obs}}^{(i)})/V_{\text{obs}}^{(i)})}{N}, \qquad (2)$$

where V_{cal} and V_{obs} are the molar volumes calculated from (1) and observed, respectively, and N is

Table 2. Comparison of molar volumes of pure NaCl, $CaCl_2$, and $LaCl_3$ melts at 900 °C. The percent departures from the recommended values are denoted in parentheses. a: (17), b: (16), c: (1).

Melt	NaCl	$CaCl_2$	$LaCl_3$
Recommended value/$cm^3\ mol^{-1}$	38.90[a]	54.61[b]	77.19[c]
This work	38.74 (− 0.41%)	54.22 (− 0.71%)	76.69 (− 0.65%)

the number of data, were 0.14% for $CaCl_2$-NaCl, 0.22% for $LaCl_3$-NaCl, and 0.20% for $LaCl_3$-$CaCl_2$.

Figure 2 shows the molar volume isotherms for the three molten binary systems at 900 °C and Fig. 3 the corresponding excess molar volumes V^E as defined by

$$V^E = V_{cal} - V_{add}, \quad (3)$$

where V_{add} refers to the additive molar volume. Evidently the deviations from additivity are positive for $LaCl_3$-NaCl, zero for $CaCl_2$-NaCl and negative for $LaCl_3$-$CaCl_2$.

Recently Bräutingan et al. [22] and Grjotheim et al. [16] have investigated the molar volume of molten $CaCl_2$-NaCl. They found a small positive deviation from the additivity with the maximum deviation at 50 mol% $CaCl_2$ in the former and at 65 mol% $CaCl_2$ in the latter work. As shown in Fig. 3, we did not find any significant deviation.

Table 3. Parameters of (1) for the three binary systems.

System	$CaCl_2$-NaCl	$LaCl_3$-NaCl	$LaCl_3$-$CaCl_2$
Parameter			
a_0	0.21464 E2	0.21464 E2	0.41953 E2
a_1	0.18800 E2	0.39016 E2	− 0.15076 E2
a_2	0.20333 E1	− 0.29153 E2	0.43181 E2
a_3	− 0.34445 E0	0.25431 E2	− 0.13299 E2
b_0	0.14731 E-1	0.14731 E-1	0.10457 E-1
b_1	− 0.29710 E-2	0.50236 E-2	0.29764 E-1
b_2	− 0.64703 E-3	0.11575 E-1	− 0.35127 E-1
b_3	− 0.65554 E-3	− 0.14336 E-1	0.11899 E-1

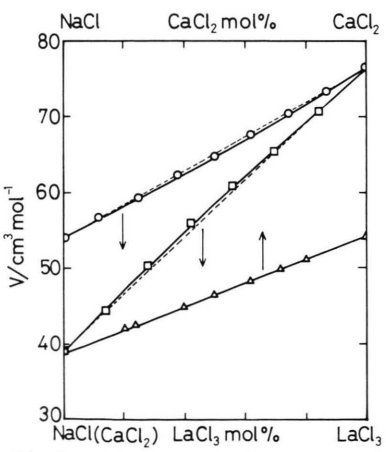

Fig. 2. Molar volume isotherms of molten $CaCl_2$-NaCl (△), $LaCl_3$-NaCl (□), and $LaCl_3$-$CaCl_2$ (○) at 900 °C. ---- additive line.

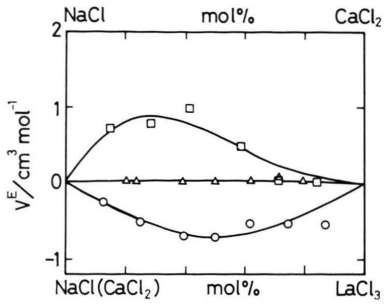

Fig. 3. Excess molar volumes of molten $CaCl_2$-NaCl (△), $LaCl_3$-NaCl (□), and $LaCl_3$-$CaCl_2$ (○) at 900 °C.

Cho and Kuroda [5] have investigated the density of molten $LaCl_3$-NaCl. The molar volumes calculated from their density data show little excess volume. Papatheodorou and Østvold [23] have presumed from the enthalpy of mixing and emf measurements on molten $LaCl_3$-NaCl that, since the partial entropy calculated from such thermodynamic data is, within experimental error, in good agreement with that given by the Temkin model [24], this molten system does not deviate significantly from a random cation mixture. However, the molar volume of $LaCl_3$-NaCl measured in the present work has a relatively large positive excess volume. In addition, the excess volume is largest at ca. 30 mol% $LaCl_3$, which is similar to the behavior of the excess volume of molten $LaCl_3$-KCl [25] where the predominance of the species $(LaCl_6)^{3-}$ is indicated by Raman spectroscopy [26, 27]. The fact appears to imply the existence of this species in molten $LaCl_3$-NaCl too.

A negative excess volume, as found for molten $LaCl_3$-$CaCl_2$, has also been found for molten $LaCl_3$-$BaCl_2$ by Stepanov and Smirnov [6]. These two systems contain alkaline earth metal ions with charge + 2. The Ca^{2+} and Ba^{2+} ions attract the chloride ions more strongly than the M^+ ions in the molten $LaCl_3$-MCl systems, which leads to a reduction of the repulsive interaction between the La^{3+} ions and the alkaline earth ions and would enable a denser packing of the ions.

Ternary melts

Molar volumes of the molten ternary system $LaCl_3$-$CaCl_2$-NaCl were measured for varying $LaCl_3$ content at constant mole ratio $CaCl_2$/NaCl, i.e., as

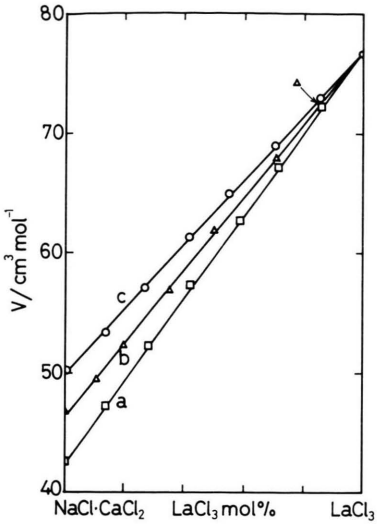

Fig. 4. Molar volume isotherms of molten quasi-binary systems at 900 °C. a: $LaCl_3$-nNaCl · $m$$CaCl_2$ (n:m = 76.2 :23.8 mol%), b: $LaCl_3$-NaCl · $CaCl_2$ (50.0:50.0), c: $LaCl_3$-nNaCl · $m$$CaCl_2$ (27.7:72.3).

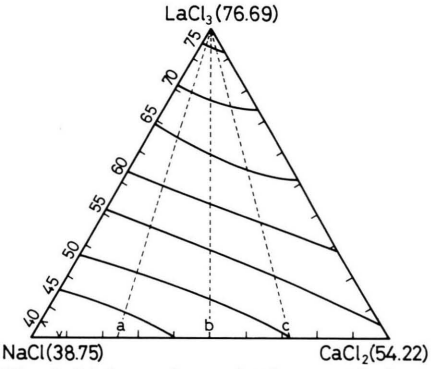

Fig. 5. Molar volume isotherms of the molten ternary $LaCl_3$-$CaCl_2$-NaCl system at 900 °C; (unit: $cm^3\,mol^{-1}$). Dashed lines *a*, *b*, and *c* indicate the quasi-binary systems measured.

Table 4. Parameters of (1) for the three quasi-binary systems.

System	*a*	*b*	*c*
Parameter			
a_0	0.25337 E2	0.31640 E2	0.36341 E2
a_1	0.45031 E2	0.36366 E2	0.57381 E1
a_2	− 0.62503 E2	− 0.35776 E2	0.22069 E2
a_3	0.48893 E2	0.24528 E2	− 0.73893 E0
b_0	0.14493 E-1	0.12711 E-1	0.11675 E-1
b_1	− 0.95247 E-2	− 0.94031 E-2	0.13986 E-1
b_2	0.56709 E-1	0.43077 E-1	− 0.78278 E-2
b_3	− 0.44684 E-1	− 0.29392 E-1	− 0.83973 E-3

Systems *a*, *b*, and *c* correspond to those in Figure 4.

three quasi-binary systems a: $LaCl_3$-NaCl·$(CaCl_2)_{3.2}$, b: $LaCl_3$-NaCl·$CaCl_2$ and c: $LaCl_3$-$(NaCl)_{2.6}$·$CaCl_2$. The obtained molar volumes were also represented by [1]. The parameters determined by the least squares method are shown in Table 4. The average percent departures for the systems a, b, and c were 0.165%, 0.270%, and 0.321%, respectively. These values are slightly larger than those of the binary systems because of some uncertainty in the determination of the composition. Figure 4 shows the composition dependence of the molar volumes of these mixtures at 900 °C. Additivity is approximately satisfied. This suggests that the opposing effects in the excess volume observed in the $LaCl_3$-NaCl and $LaCl_3$-$CaCl_2$ systems are cancelled out in the ternary mixtures.

Figure 5 shows roughly the molar volume isotherms of the $LaCl_3$-$CaCl_2$-NaCl system at 900 °C according to the isotherms of the three binary and the three quasi-binary mixtures.

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