Molar Volumes of $LiNO_3$-$Ca(NO_3)_2$ and $LiNO_3$-$Ba(NO_3)_2$ Melts

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The molar volumes of molten $LiNO_3$-$Ca(NO_3)_2$ and $LiNO_3$-$Ba(NO_3)_2$ mixtures were measured dilatometrically and are represented as functions of composition and temperature.

The densities of several molten binaries of calcium and barium nitrate with alkali metal nitrates have been measured [1]. Binaries with lithium nitrate are not among these because of the low solubility of these alkaline earth nitrates in lithium nitrate and the thermal lability of lithium nitrate. However, it is known that both molten binaries exist in a limited composition and temperature range [2]. The density data of the melts are indispensable in the evaluation of the electronic polarizability [3]. Our interest in the polarization phenomenon induced us to measure the molar volumes of $LiNO_3$-$Ca(NO_3)_2$ and $LiNO_3$-$Ba(NO_3)_2$ melts.

$LiNO_3$ and $Ba(NO_3)_2$ of analytical reagent grade were dried by heating at about 200 °C under reduced pressure for 8 hours. Anhydrous $Ca(NO_3)_2$ was prepared from $Ca(NO_3)_2$

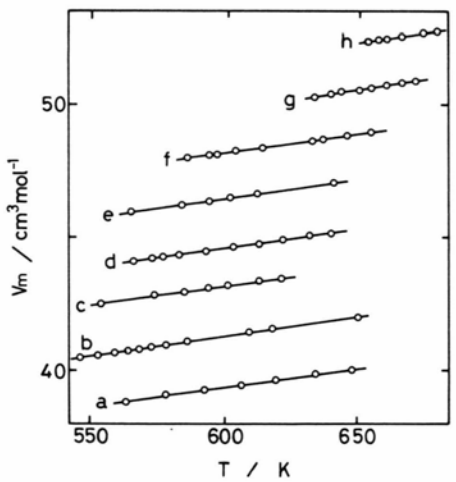

Fig. 1. Molar volumes of molten $LiNO_3$-$Ca(NO_3)_2$ mixture. Circles indicate the observed values and solid lines those calculated from (1). $Ca(NO_3)_2$ mol%, a: 0.0, b: 5.1, c: 10.4, d: 15.0, e: 20.0, f: 25.0, f: 29.7, g: 34.9.

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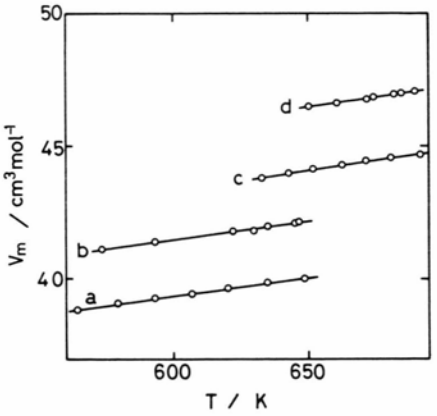

Fig. 2. Molar volumes of molten $LiNO_3$-$Ba(NO_3)_2$ mixture. Circles and solid lines have the same meaning as in Figure 1. $Ba(NO_3)_2$ mol%, a: 0.0, b: 5.0, c: 9.9, d: 15.0.

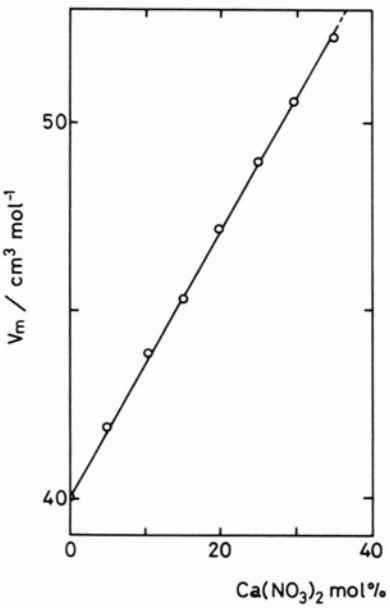

Fig. 3. Molar volume isotherm of molten $LiNO_3$-$Ca(NO_3)_2$ mixture at 650 K.

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

System	$LiNO_3$-$Ca(NO_3)_2$	$LiNO_3$-$Ba(NO_3)_2$
a_0	0.31160 E2	0.31160 E2
a_1	0.16516 E2	0.10491 E2
a_2	−0.16191 E2	−0.16347 E2
a_3	0.10064 E2	0.12057 E2
b_0	0.13614 E-1	0.13624 E-1
b_1	−0.66032 E-2	−0.50119 E-2
b_2	0.26759 E-1	0.19896 E-1
b_3	−0.17303 E-1	−0.14506 E-1

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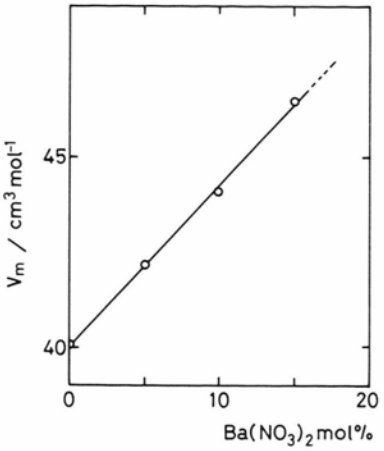

Fig. 4. Molar volume isotherm of molten $LiNO_3$-$Ba(NO_3)_2$ mixture at 650 K.

$\cdot 4H_2O$ by heating at 230 °C in vacuo for a day according to [4]. It was confirmed by DTA and TG that in this way the water was completely removed. Known amounts of the samples were weighed in a glove box filled with dried N_2 gas and then melted in fused silica under N_2 atmosphere at a temperature somewhat above liquidus given in [2]. After mixing by bubbling with N_2 gas, the melt was quenched to prevent segregation. The molar volumes of the molten mixtures were meassured dilatometrically under N_2 atmosphere by a procedure described in detail in [5].

Our results are shown in Figs. 1 and 2. They are restricted to 34.9 mol% $LiNO_3$ and 15.0 mol% $LiNO_3$, respectively, because of the thermal decomposition of $LiNO_3$. The molar volumes of pure molten $LiNO_3$ are in excellent agreement with those calculated from density data reported by Murgulescu and Zuca [6]. The molar volume for the mixtures can expresses as

$$V_m = \sum_{n=0}^{3} a_n X^n + \left(\sum_{n=0}^{3} b_n X^n \right) T, \qquad (1)$$

where T is the temperature in K and X the mole fraction of the alkaline earth nitrate. The coefficients, as determined by a least squares fit, are giving in Table 1. In the calculation, reduced mole fractions were used, i.e., the largest mole fraction measured was taken to be unity. The solid lines in Figs. 1 and 2 are obtained from (1). The standard errors as defined in [7] were 0.67 E-1 for $LiNO_3$-$Ca(NO_3)_2$ and 0.16 E-1 for $LiNO_3$-$Ba(NO_3)_2$.

Figures 3 and 4 show the molar volumes of these mixtures at 650 K. The molar volumes of the molten binaries of the present alkaline earth nitrates with alkali nitrates having larger cationic radii exhibit positive deviation from additivity [8, 9]. This is not observed for the two $LiNO_3$ systems in the range of our measurements.

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