Molar Volumes of $LaCl_3$ - MCl (M = Li, Rb, and CS) Melts

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Z. Naturforsch. **42 a,** 1418 – 1420 (1987); received July 22, 1987

The molar volumes of $LaCl_3$–MCl (M = Li, R, and Cs) melts were measured at 800 and 900 °C, and the molar volume isotherms at 900 °C are represented. They show positive deviations from additivity with the maximum at ca. 30mol% $LaCl_3$. The excess molar volume was found to increase with increasing radius of the M^+ cation.

Introduction

We reported that the molar volumes of $LaCl_3$–NaCl [1] and $LaCl_3$–KCl [2] melts show positive deviations from additivity with the maximum deviation at ca. 30 mol% $LaCl_3$. Smirnov and Stepanov found no significant deviation for $LaCl_3$–LiCl melts [3] and a positive deviation with the maximum at ca. 75 mol% $LaCl_3$ for $LaCl_3$–CsCl melts [4]. Complex formation by the reaction $LaCl_3 + 3\,MCl \rightarrow LaCl_6^{3-} + 3\,M^+$, as indicated by conductivity [5] and Raman [6] measurements, suggests a maximum molar volume deviation from additivity at about 25 mol% $LaCl_3$. This prompted us to remeasure the molar volumes of molten $LaCl_3$–MCl (M = Li and Cs) and to measure that of molten $LaCl_3$–RbCl.

Experimental

LiCl, RbCl, and CsCl of analytical reagent grade were dried by heating at 50 °C below their melting points under a vacuum of 0.13 Pa for 8 hours and then melted. After solidification the chemicals were stored in ampoules. $LaCl_3$ was prepared and purified as described in [7]. The mole ratios of the mixtures were checked by chelate titration. The molar volumes were measured as described in [1].

Results and Discussion

Single melts

The densities given in [8], [9], and [9] for molten LiCl, RbCl, and CsCl, respectively, have been recommended by Janz et al. [10]. The molar volumes at 800 and 900 °C measured in the present work are listed in Table 1 together with those calculated from the recommended data. Our results yield smaller values than the recommended ones, but the departures are within 1.5%. The molar volume of molten $LaCl_3$ was as in [1].

Binary melts

The measured molar volumes were expressed as functions of both temperature and mole fraction as

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

Table 1. Molar volumes of LiCl, RbCl, and CsCl melts at 800 and 900 °C (the recommended data/this work). The percent deviations from the recommended values are denoted in parentheses. a: [8], b: [9].

Melt	LiCl^a	RbCl^b	CsCl^b
800 °C	29.86/29.52 (−1.14)	55.64/55.46 (−0.32)	64.10/63.60 (−0.78)
900 °C	30.80/30.34 (−1.50)	58.00/57.71 (−0.50)	66.81/66.27 (−0.81)

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Table 2. Parameters of (1) for the three binary systems. m is the number of experimental data points.

System	$LaCl_3$–LiCl	$LaCl_3$–RbCl	$LaCl_3$–CsCl
Parameter			
a_0	0.20665E2	0.31354E2	0.34894E2
a_1	0.70633E1	0.89781E2	0.26672E2
a_2	0.81860E2	−0.21042E3	0.82209E1
a_3	−0.67173E2	0.13170E3	−0.27372E2
b_0	0.82494E-2	0.22463E-1	0.26747E-1
b_1	0.36917E-1	−0.51809E-1	−0.28804E-2
b_2	−0.75978E-1	0.16227	−0.28835E-1
b_3	0.60085E-1	−0.10365	0.34241E-1
m	125	74	92

where V_m is the molar volume in $cm^3 mol^{-1}$, X the mole fraction of $LaCl_3$, and T the absolute temperature. The parameters a_n and b_n, as determined by a least squares regression of all the obtained data, are listed in Table 2. The standard errors of V_m, defined as

$$s = \sqrt{\sum^{m} (Z_e - Z)^2/(m-q)}\,, \tag{2}$$

where Z_e is the experimental value, Z the corresponding value calculated from the least squares fit, m the number of experimental data points, and q the number of coefficient in the fitting equation, were 0.38 for $LaCl_3$–LiCl, 0.34 for $LaCl_3$–RbCl, and 0.34 for $LaCl_3$–CaCl.

Figure 1 shows the molar volume isotherms for the three molten binary systems at 900 °C and Fig. 2 the corresponding excess molar volumes, V^E, as defined by

$$V^E = V_{cal} - V_{add} \tag{3}$$

with V_{cal} the value of V_m according to (1) and

$$V_{add} = a_0 + \left(\sum_{n=1}^{3} a_n X\right) + \left[b_0 + \left(\sum_{n=1}^{3} b_n X\right)\right] T. \tag{4}$$

In analogy with the $LaCl_3$–NaCl [1] and $LaCl_3$–KCl [2] melts, the maxima of the deviation from additivity are again found at about 30 mol% $LaCl_3$, although there are appreciable differences in their magnitude. Raman spectroscopy of molten $LaCl_3$–MCl (M = Na [6, 11], K [6, 11, 12], and Cs [6]) mixtures did indicate that octahedral $LaCl_6^{3-}$ is predominant at 25 mol% $LaCl_3$. The formation of such a large complex anion can well be the reason for an appreciable positive V^E with a maximum at about 30 mol% $LaCl_3$.

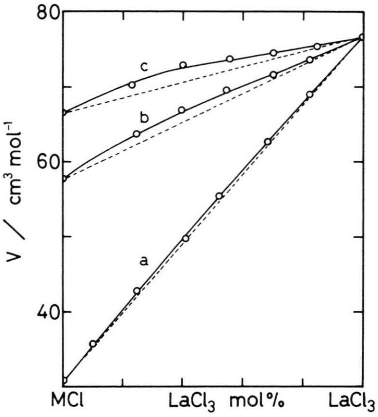

Fig. 1. Molar volume isotherms of molten $LaCl_3$–LiCl (a), $LaCl_3$–RbCl (b), and $LaCl_3$–CsCl (c) at 900 °C. Dotted lines indicate additivity.

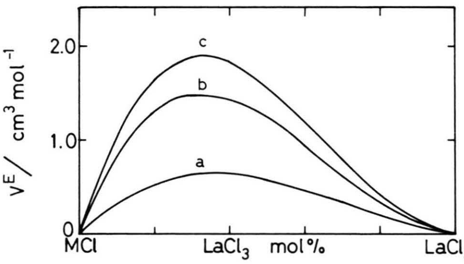

Fig. 2. Excess molar volumes of $LaCl_3$–LiCl (a), $LaCl_3$–RbCl (b), and $LaCl_3$–CsCl (c) melts at 900 °C.

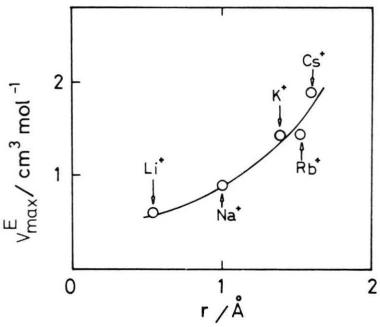

Fig. 3. Maximum excess molar volumes vs. alkali ion radii [13]. The values of $LaCl_3$–NaCl and $LaCl_3$–KCl were taken from [1] and [2].

In Fig. 3 the maximum excess volumes are plotted against the ionic radii of the alkali metal ions [13]. The evident correlation suggests that the formation of the complex $LaCl_6^{3-}$ becomes the more pronounced the larger the alkali ion, i.e., the weaker the attraction of the chloride ions by the alkali ions.

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