The Molar Volume of Molten Mixtures of MCl-LnCl$_2$ (M = Alkali Metals, Ln = Lanthanoides)

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Z. Naturforsch. **63a,** 203 – 209 (2008); received July 16, 2007

Presented at the EUCHEM Conference on Molten Salts and Ionic Liquids, Hammamet, Tunisia, September 16 – 22, 2006.

Empirical equations for the density and molar volume of molten binary mixtures of MCl-LnCl$_2$ and MCl-MeCl$_2$ (M = alkali metals; Ln = lanthanoides; Me = Ca, Sr, Ba) based on the density of individual components are suggested. The equations, taking into account the deviations of the molar volumes from their additive values, are applicable to all binary systems involving known rare earth dichlorides.

Key words: Molten Salts; Rare Earth Elements; Dichlorides; Density.

1. Introduction

Rare earth ions of molten salts are not always trivalent but in some cases also divalent. Until now, solutions of LnCl$_2$ (Ln = lanthanoides) in molten chlorides are scantily studied. No information on the density of molten MCl-LnCl$_2$ (M = alkali metals) mixtures was found in the literature.

The estimation of the density (molar volume) molten MCl-LnCl$_3$ mixtures has been developed in [1, 2]. The density of molten alkali chlorides has often been measured with a precision of ±0.5% and better [3, 4]. Some of the salts are recommended as standards for calibrations [5, 6].

The aim of the present work is to develop a procedure of computing the density of molten MCl-LnCl$_2$ (M = Li, Na, K, Rb, Cs; Ln = all lanthanoides), based on the knowledge of the densities of the individual salts.

It is well known that the density is not additive. The density of mixtures calculated by

$$d_{\text{mix}} = x_1 \cdot d_1 + x_2 \cdot d_2, \qquad (1)$$

with x_1 and x_2 being the mole fractions, exhibits up to 10% deviation from the real values.

The molar volume $V_{\text{m(mix)}} = M_{\text{mix}}/d_{\text{mix}}$ is much more an additive feature. Calculations made in terms of the equation

$$V_{\text{m(mix)}} = x_1 \cdot V_{\text{m}1} + x_2 \cdot V_{\text{m}2} \qquad (2)$$

are more precise.

Nevertheless, molar volumes of molten binary salts with essential difference in the properties of the components also reveal appreciable deviations of V_{m} from additivity.

For a more exact computation of the molar volumes of molten binary mixtures the following equation was proposed [1, 2]:

$$V_{\text{m(mix)}} = (x_1 \cdot V_{\text{m}1} + x_2 \cdot V_{\text{m}2}) \cdot (1 + K_1 \cdot K_2 \cdot K_3), \qquad (3)$$

where K_1 is the correction describing the shape of the excess molar volume curve, K_2 is the correction taking into account the excess molar volume increase in going from the LiCl-LnCl$_2$ systems to the CsCl-LnCl$_2$ ones, and K_3 is the correction for the temperature effect on the excess molar volume.

The multiplicative form of corrections $K_1 \cdot K_2 \cdot K_3$ was chosen instead of the sum $K_1 + K_2 + K_3$ to simplify its presentation. Indeed the total correction ($K_1 \cdot K_2 \cdot K_3$ or $K_1 + K_2 + K_3$) should be equal zero when [LnCl$_2$] = 0% or = 100% and it reaches its maximum somewhere in between. In case of the multiplicative form it is sufficient, if only one of the corrections is a function of concentration: $K_1 = f([\text{LnCl}_2])$. Then the other ones

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are expressible as simple numerical values or functions independent of the concentration.

indent In the present work (3) is adopted for the molar volume of molten MCl-LnCl$_2$ mixture calculations, and the dimensionless coefficients K_1, K_2 and K_3 are evaluated.

2. Results and Discussion

Because of lacking experimental data on the density of the systems under consideration, it is necessary to find other approaches to estimate the corrections K_1, K_2 and K_3. Our approach bases on the assumption of fairly close analogy of the volume properties of the melts containing divalent rare earth chlorides and alkali earth chlorides. Indeed, it is well known that rare earth dichlorides are similar to alkali earth dichlorides in many respects [7–9]. Their cations have an equal charge and nearly the same radius [10]. The chlorides have similar melting points and structures [11, 12]. Thus the following assumption is reasonable: *The molten MCl-MeCl$_2$ and MCl-LnCl$_2$ (Me = Ca, Sr, Ba) mixtures have similar molar volume relative deviations from additivity.* Literature data on the density (molar volume) of MCl-MeCl$_2$ mixtures are rather numerous [4, 13–29]. However, simple juxtaposing and averaging does not allow us reach definite conclusions on excess volumes of the systems under consideration. These results are too contradictory. For example, in [13] the curve of relative deviations from additivity in the KCl-CaCl$_2$ system at 1173 K was found to have a complicate shape with sharp extremes, maximum positive deviation $\delta_{\max(+)} = 0.8\%$ and maximum negative deviation $\delta_{\max(-)} = -0.45\%$. In [14] the curve of relative deviations from additivity in the KCl-BaCl$_2$ system at the same temperature has an oscillatory character and lies mainly in the negative region. Deviations are $\delta_{\max(+)} = 0.77\%$, $\delta_{\max(-)} = -2.1\%$. In [21] KCl mixtures with CaCl$_2$, SrCl$_2$ and BaCl$_2$ were studied. In all cases deviations were very positive and approximately identical, namely $\delta_{\max(+)} = 9-10\%$. Such large deviations are possible in systems with very strong interaction of the components. For example even in system the CsCl-LaCl$_3$ $\delta_{\max(+)}$ does not exceed 5–6% [1, 24]. In [22] systematic measurements of the densities of molten MCl-SrCl$_2$ (M = Li, Na, K, Rb, Cs) systems were performed. Negative deviations were found in LiCl-SrCl$_2$, complicate relationships in subsequent systems and additive behaviour in CsCl-SrCl$_2$.

Table 1. Cationic radii (r in nm [10]) and ionic potentials (Z in nm^{-1}) of several ions.

Ion	r	Z	Ion	r	Z
Mg^{2+}	0.072	27.78	Nd^{2+}	0.123	16.26
Ca^{2+}	0.100	20.00	Pm^{2+}	0.121	16.53
Sr^{2+}	0.118	16.95	Sm^{2+}	0.119	16.81
Ba^{2+}	0.135	14.81	Eu^{2+}	0.117	17.09
Mn^{2+}	0.083	24.10	Tm^{2+}	0.103	19.42
Pb^{2+}	0.119	16.81	Yb^{2+}	0.102	19.61

All efforts to find any tendency in a whole array of data were futile. First of all it was necessary to develop criteria of data sorting to select trustworthy values and to reject the indubitable ones. Actually a part of the conclusions of [24] were adopted as the criteria:

In molten MCl-MeCl$_2$ binary systems 1. the excess molar volume (V_{ex}) is positive; 2. V_{ex} increases from LiCl to CsCl; 3. maximal relative deviations of V_{ex} from additivity do not exceed 3–5%.

Most of the data were excluded according to these criteria. Unfortunately, even values quoted in the reference book [4] were improper from the point of view of the criteria. Nonsystematic works with one-off results also were useless to discover any regularity in spite of the fact that they meet these criteria. Finally, only three works [19, 24, 25] were selected for quantitative estimations, which contain systematic and consistent data on the density of MCl-CaCl$_2$ and MCl-SrCl$_2$ systems. These salts are best-suited analogues to MCl-LnCl$_2$ systems due to the proximity of the Ca^{2+}, Sr^{2+} and Ln^{2+} ionic radii (r) [10] and ionic potentials (Z). This is evident from Table 1, where the ionic radii and ionic potentials of alkali earth, rare earth and some other divalent elements for comparison are listed. The ionic potential was calculated according to $Z = q/r$, were q is charge of a cation in elementary charge units ($q = 1$ for alkali metals and $q = 2$ for dipositive cations), and r is the radius of a cation in nm according to Shannon [10]. Ionic potentials are conventional measures of the interaction of cations with chloride ions.

The ionic potentials of all Ln^{2+} lie between the ionic potentials of Ca^{2+} and Ba^{2+}. The value of Z of "light" ions (Nd^{2+}, Pm^{2+}, Sm^{2+} and Eu^{2+}) is close to that of Sr^{2+}, while the ionic potential of "heavy" ions (Tm^{2+}, Yb^{2+}) is approximately that of Ca^{2+}. It was an additional argument in favour of the choice of these systems as the closest analogues of MCl-LnCl$_2$ systems. The values of V_{ex} relative deviations [19] are on average 0.5% lower than those of Stepanov [24, 25]. Evaluation of the K_1, K_2 and K_3 correction coefficients was based on the analysis of concentration and tem-

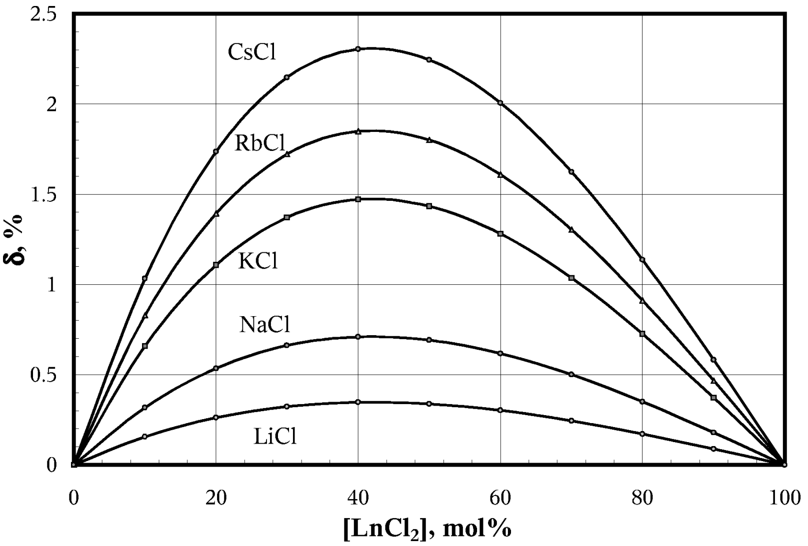

Fig. 1. Molar volume relative deviations from additivity (δ, %) of molten MCl-LnCl$_2$ mixtures at 1173 K.

perature dependences of the relative deviations δ of the experimental molar volume (V_m) from its additive values V_{add}: $\delta = (V_m - V_{add})/V_{add}$. Using the above-mentioned experimental data on MCl-CaCl$_2$ and MCl-SrCl$_2$ systems, the equation for K_1 was deduced:

$$\begin{aligned} K_1 &= 7.417088 \cdot 10^{-6} \\ &+ 7.71785 \cdot 10^{-2} \cdot [\mathrm{LnCl_2}] \\ &- 1.16893 \cdot 10^{-3} \cdot [\mathrm{LnCl_2}]^2 \\ &+ 3.969366 \cdot 10^{-6} \cdot [\mathrm{LnCl_2}]^3, \end{aligned} \tag{4}$$

where [LnCl$_2$] is the concentration in mol%.

The correction K_1 describes the shape of molar volume relative deviations (see Fig. 1). The curve of the excess volume of the NaCl-SrCl$_2$ system [24] was taken as a standard. The coefficients are fitted in such a way that in KCl-LnCl$_2$ systems at 1173 K the other coefficients K_2 and K_3 are equal 1. It is presumed that maximum deviations from additivity occur when [LnCl$_2$] = 42 mol%. It is rigorously impossible to compute the value 42 mol% based only on available experimental data. Their scattering is so large that simple averaging does not give a statistically valid result. On the other hand strictly speaking the maximum position slightly depends on both alkali cation and Me^{2+} (or Ln^{2+}). Therefore it is more correct to describe some range of maximal values. This range should be rather narrow because of the uniformity of the systems under consideration. Even if the uncertainty of the maximum position is 35 – 55 mol% MeCl$_2$, it leads to small errors, ~ 0.05%.

As it is well known in molten MCl-MeCl$_2$ mixtures, diluted on MeCl$_2$, divalent cations form complexes like [MeCl$_4$]$^{2-}$ with the coordination number four [30 – 33]. With increasing content of MeCl$_2$ the character of complex formation changes and the extremes of the excess functions are in the range 40 – 45 mol% of MeCl$_2$. The fact is confirmed by many examples. For instance maxima of the activation energy and excess molar conductivity of MCl-CaCl$_2$ [34] and MCl-EuCl$_2$ [35] lie in this range. The maximum of the mixing enthalpy in the MCl-EuCl$_2$ system is observed near 40 mol% of EuCl$_2$ [36] (see Fig. 2).

Relative deviations increase from LiCl-LnCl$_2$ mixtures to CsCl-LnCl$_2$ ones because interactions between components (MCl and LnCl$_2$) increase in the same order. The effect of alkali cation size on the relative deviations of excess volume accounts for the K_2 correction (K_2 = 0.236 for LiCl; 0.482 for NaCl; 1.00 for KCl; 1.257 for RbCl; and 1.566 for CsCl). The experimental data used for K_2 estimation are plotted in Figure 3. The values smoothly elevate with increasing cationic radius. The K_2 correction can also be calculated according to

$$K_2 = 0.1284334 - 4.595909 \cdot r + 79.06963 \cdot r^2, \tag{5a}$$

where r is the radius of the alkali cation in nm according to Shannon [10]. This equation is especially convenient for ternary systems with two alkali cations [for example, (NaCl-KCl)-EuCl$_2$].

For example for (LiCl-KCl)$_{eut}$-LnCl$_2$ mixtures K_2 = 0.476, for (NaCl-KCl)-LnCl$_2$ K_2 = 0.7155. For the

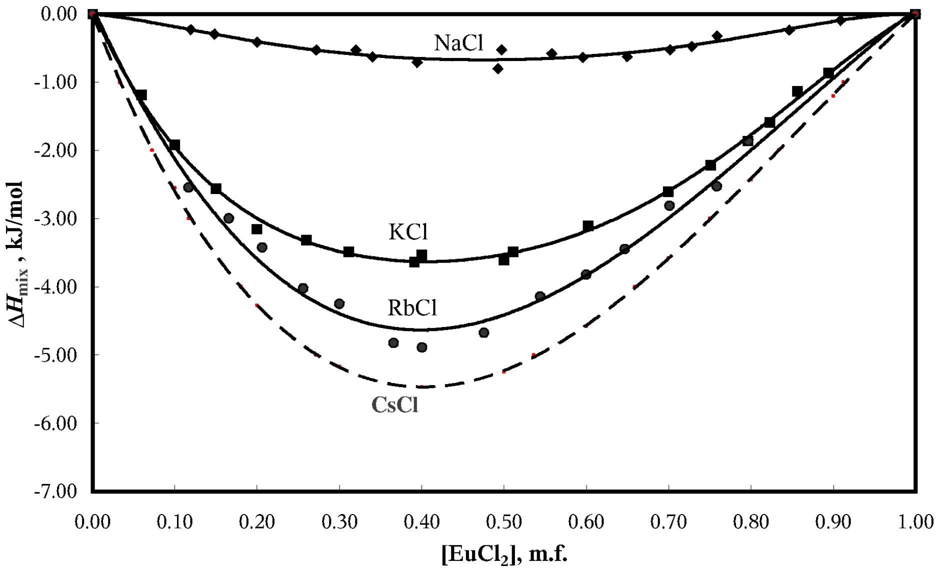

Fig. 2. Molar enthalpies of mixing (ΔH_{mix}) of liquid MCl-EuCl$_2$ systems at 1138 K [36].

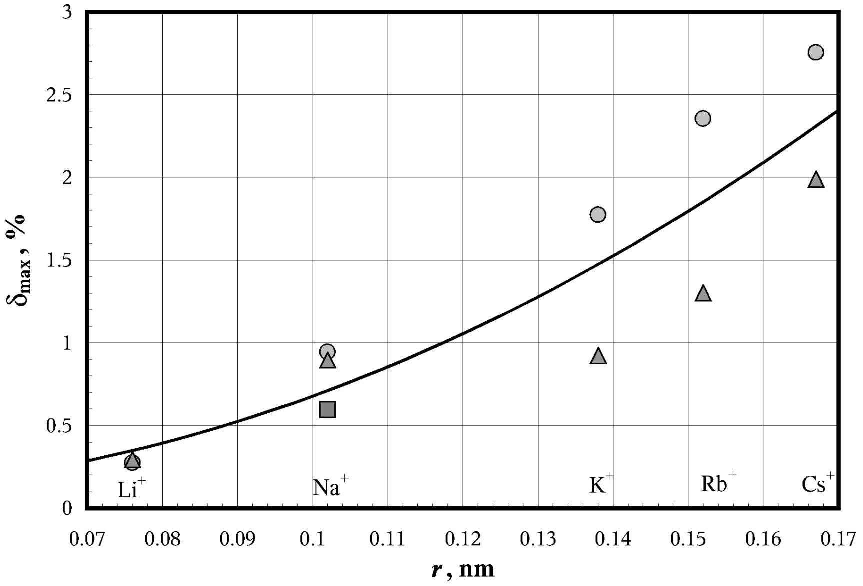

Fig. 3. Dependence of maximum relative deviations from additivity of molar volumes of MCl-MeCl$_2$ molten mixtures on the cationic radius of alkali metals (data for calculations of K_2 correction). ● - [24] on MCl-SrCl$_2$ system; ■ - [19] on MCl-SrCl$_2$ system; ▲ - [19] on MCl-CaCl$_2$ system.

aims of polynomial extrapolation (5a) is unusable. Correct extrapolation is provided by

$$\ln(K_2) = 2.0136 - 0.2759 \cdot Z, \tag{5b}$$

where Z is the ionic potential of salt solvent. For example, for (NaCl-CaCl$_2$)-LnCl$_2$ molten systems $K_2 = 0.12$.

With increasing temperature the systems become simpler and deviations of the molar volume from additivity diminish. The effect is described by the correction K_3:

$$K_3 = 2.904716 - 2.155681 \cdot 10^{-3} \cdot T + 4.511571 \cdot 10^{-7} \cdot T^2, \tag{6}$$

where T is the temperature in K.

The value of K_3 is approximately $-11\%/100$ K, i. e., deviations δ reduce by 11% per each 100 degrees. It should be expected that the molar volumes of the individual molten LnCl$_2$ are close to each other because increasing of the molar mass from Nd to Yb

Table 2. Density ($d = a + b \cdot T$) and molar volume ($V_\mathrm{m} = A + B \cdot T$) of molten MCl-SmCl$_2$ mixtures, calculated according to (3)–(7) (MCl = NaCl-CaCl$_2$; LiCl-KCl; NaCl-KCl; KCl and CsCl). Densities of MCl were adopted from [4], molar volumes [V_m(SmCl$_2$) = V_m(EuCl$_2$)] from [37].

[SmCl$_2$], mol%	a	$-b \cdot 10^3$	d (1173 K), g/cm^3	A	$B \cdot 10^2$	V_m (1173 K), cm^3/mol
			(0.48NaCl-0.52CaCl$_2$)$_\mathrm{eut}$			
0	2.3718	0.4905	1.796	32.449	1.254	47.16
10	2.9477	0.7741	2.040	27.534	1.763	48.23
20	3.5631	1.1000	2.273	22.591	2.275	49.28
30	4.2138	1.4640	2.497	17.624	2.787	50.32
40	4.8963	1.8625	2.713	12.639	3.300	51.36
50	5.6073	2.2923	2.921	7.6413	3.814	52.38
60	6.3437	2.7503	3.121	2.6340	4.327	53.40
70	7.1027	3.2337	3.313	−2.3788	4.841	54.41
80	7.8816	3.7399	3.500	−7.3939	5.354	55.42
90	8.6777	4.2664	3.679	−12.409	5.867	56.42
100	8.8234	4.2359	3.854	−17.421	6.38	57.42
			(0.59LiCl-0.41KCl)$_\mathrm{eut}$			
0	2.0286	0.5268	1.411	22.754	1.418	39.40
10	2.7355	0.8440	1.746	18.960	1.906	41.33
20	3.4656	1.2055	2.052	15.083	2.399	43.23
30	4.2112	1.6007	2.335	11.138	2.894	45.10
40	4.9662	2.0219	2.596	7.1362	3.392	46.94
50	5.7262	2.4627	2.840	3.0917	3.891	48.74
60	6.4875	2.9181	3.068	−0.98487	4.390	50.52
70	7.2471	3.3840	3.282	−5.0832	4.889	52.27
80	8.0023	3.8568	3.483	−9.1940	5.387	54.01
90	8.7504	4.3335	3.674	−13.309	5.884	55.72
			NaCl-KCl (1 : 1)			
0	2.1314	0.5679	1.465	25.509	1.693	45.38
10	2.7393	0.8424	1.751	21.597	2.148	46.81
20	3.3822	1.1591	2.023	17.537	2.611	48.17
30	4.0575	1.5140	2.282	13.357	3.078	49.48
40	4.7629	1.9038	2.531	9.0828	3.549	50.73
50	5.4961	2.3254	2.771	4.7367	4.023	51.93
60	6.2548	2.7759	3.002	0.33976	4.496	53.09
70	7.0364	3.2526	3.225	−4.0897	4.969	54.21
80	7.8382	3.7527	3.441	−8.5354	5.441	55.30
90	8.6570	4.2733	3.651	−12.983	5.912	56.37
			KCl			
0	2.1359	0.5831	1.452	28.080	1.982	51.35
10	2.6689	0.8209	1.706	24.122	2.400	52.30
20	3.2446	1.0998	1.955	19.927	2.831	53.15
30	3.8647	1.4200	2.200	15.543	3.269	53.90
40	4.5305	1.7819	2.442	11.011	3.712	54.57
50	5.2428	2.1854	2.681	6.3703	4.159	55.16
60	6.0019	2.6305	2.919	1.6541	4.606	55.70
70	6.8076	3.1168	3.155	−3.1071	5.053	56.18
80	7.6588	3.6434	3.390	−7.8874	5.498	56.62
90	8.5536	4.2089	3.623	−12.665	5.941	57.03
			CsCl			
0	3.7692	1.065	2.520	35.016	2.709	66.81
10	4.0710	1.2463	2.609	30.947	3.034	66.55
20	4.4224	1.4611	2.709	26.382	3.381	66.06
30	4.8263	1.7124	2.818	21.429	3.744	65.37
40	5.2868	2.0034	2.938	16.182	4.118	64.51
50	5.8079	2.3378	3.067	5.8079	2.338	63.51
60	6.3944	2.7198	3.207	5.1372	4.881	62.40
70	7.0511	3.1537	3.355	−0.52103	5.262	61.22
80	7.7828	3.6440	3.513	−6.1944	5.640	59.98
90	8.5941	4.1951	3.679	−11.839	6.013	58.70

is nearly compensated by density increasing in the same order. Therefore replacing of one Ln^{2+} by another cation leads only to insignificant changes of excess molar volumes of MCl-$LnCl_2$ mixtures, and no special correction in going from Nd^{2+} to Yb^{2+} is required.

As an example for using (3) the temperature dependences of density and molar volume of molten quasibinary MCl-$SmCl_2$ mixtures (M = NaCl-$CaCl_2$; LiCl-KCl; NaCl-KCl; KCl and CsCl) were calculated. The results are shown in Table 2. The calculations were carried out in the temperature range 1023 – 1123 K. The densities of alkali chlorides were taken from [4]. The density of molten $SmCl_2$ was estimated assuming $V_m(SmCl_2) = V_m(EuCl_2)$. There is only one publication on the density of molten rare earth dichlorides. In [37] the molar volume of molten $EuCl_2$ was found as:

$$V_m(EuCl_2) = -17.421 + 0.0638 \cdot T \quad (1153 < T/K < 1273); \tag{7}$$

then

$$d(SmCl_2) = 8.823 - 4.24 \cdot 10^{-3} \cdot T.$$

3. Conclusion

The general equation (4) is universal and applicable in many cases. The accuracy of the equation depends on the accuracy of the coefficients K_1, K_2, K_3, the number of which is variable. For example using additional coefficients, it is possible to take into account the shift of the maximum position of the relative deviations depending on the temperature and/or composition of the molten mixture.

The uncertainty of the equations suggested for calculating the density of MCl-$LnCl_2$ molten mixtures does not exceed 1% above the uncertainty of the density of individual components.

Since (4) – (6) were developed based on experimental data on the density of the MCl-$MeCl_2$ (Me = Ca, Sr, Ba) systems the results are valid for these systems. Thus the method to calculate the density (molar volume) of two classes of molten mixtures, namely MCl-$MeCl_2$ and MCl-$LnCl_2$, was developed.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (project No. 04-03-96103).

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