Molar Volumes and Molar Excess Volumes of Molten Alkali Chloride + Silver Chloride Mixtures

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Dedicated to Professor Dr. Rolf Haase on the occasion of his 65th birthday

Measurements of the densities (and with these of the molar volumes and the excess volumes) of the molten salt systems LiCl + AgCl, NaCl + AgCl, KCl + AgCl, RbCl + AgCl, and CsCl + AgCl as functions of composition and temperature from the liquidus curve up to 1200 K are reported. It is shown that a linear relation with the volume fraction fits the measured densities of the alkali chloride + silver chloride mixtures better than one with the mole fraction.

Binary molten salt mixture show very often no ideal behaviour in their molar volumes [1, 2]. Thus it is impossible to calculate the molar volumes of the mixtures from those of the pure salts. On the other hand the knowledge of the molar volumes is necessary for many experimental and theoretical considerations.

As it is difficult to measure molar volumes directly, they are usually determined indirectly by density measurements, for which some approved methods are available. In this paper the densities, and so the molar volumes, of the alkali chloride + silver chloride systems LiCl + AgCl, NaCl + AgCl, KCl + AgCl, RbCl + AgCl, and CsCl + AgCl are presented.

The ideal molar volume $\bar{V}_{\text{id}}$ of a binary molten salt is given by the densities ϱ_1 and ϱ_2 of the pure components

$$\bar{V}_{\text{id}} = x_1 \frac{M_1}{\varrho_1} + x_2 \frac{M_2}{\varrho_2}, \qquad (1)$$

where x_1 and x_2 denote the mole fractions of the components 1 (alkali chloride) and 2 (silver chloride), and M_1 and M_2 their molar weights. The real molar volume $\bar{V}_{\text{exp}}$ can be determined from the measured density ϱ_{exp} of the mixture

$$\bar{V}_{\text{exp}} = \frac{x_1 M_1}{\varrho_{\text{exp}}} + \frac{x_2 M_2}{\varrho_{\text{exp}}}. \qquad (2)$$

The molar excess volume $\bar{V}^{\text{E}}$ is the difference of (1) and (2):

$$\bar{V}^{\text{E}} = \bar{V}_{\text{exp}} - \bar{V}_{\text{id}}. \qquad (3)$$

Our experimental setup [3] is similar to Bloom's device [4], based on the Archimedies axiom, and is a realization of the "sinker method". The measurements were carried out at given compositions as functions of temperature. The lowest temperature was given by the phase diagram of the respective system [5]; the highest temperature was 1200 K (930 °C).

The alkali chlorides, of p.A. quality, were delivered by MERCK and the silver chloride by DEGUSSA. All salts were dried 24 h at 60 °C under vacuum – the hygroscopic LiCl 48 h at 100 °C – before being used.

Results

At a given composition, the densities are a linear function of temperature:

$$\varrho = A + BT.$$

The axis intercept A and the slope B depend on the composition. Both dependencies can best be described by cubic equations. Thus the density as function of temperature and composition results from a combination of two cubic equations:

$$\varrho(x_2, T) = (a + b x_2 + c x_2^2 + d x_2^3) + (a' + b' x_2 + c' x_2^2 + d' x_2^3)\, T. \qquad (4)$$

Here a, b, c, d, a', b', c', and d' are system specific constants, which are listed in Table 1.

As the densities of the pure components are known [1] and also calculable with (4), the molar excess volumes can be determined with (1), (2), and (3). These $\bar{V}^{\text{E}}$ of all systems are listed in Table 2 for a temperature of 1075 K.

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Table 1. Constants for the calculation of the densities of the molten alkali chloride + silver chloride mixtures, depending on temperature and composition.

	LiCl + AgCl	NaCl + AgCl	KCl + AgCl	RbCl + AgCl	CsCl + AgCl
a (g cm^{-3})	1.87583	2.14526	2.12547	3.08085	3.76102
b (g cm^{-3})	4.22727	3.04521	2.52535	1.72270	1.20341
c (g cm^{-3})	−0.68777	0.47415	0.71340	0.30917	−0.21383
d (g cm^{-3})	0.18288	−0.11201	0.19279	0.42768	0.79912
$a' \cdot 10^{+4}$ (g cm^{-3} K^{-1})	−4.25644	−5.47606	−5.74595	−8.45830	−10.5269
$b' \cdot 10^{+4}$ (g cm^{-3} K^{-1})	−8.96975	−5.97629	−6.12836	−4.35437	−3.26651
$c' \cdot 10^{+4}$ (g cm^{-3} K^{-1})	5.09725	−0.50862	−2.02796	−0.34763	2.74202
$d' \cdot 10^{+4}$ (g cm^{-3} K^{-1})	−1.26046	2.55160	4.45813	3.85404	1.65639

All investigated systems have a positive excess volume. Plotting them versus the mole fraction shows that the maximum value of all systems is at $x_2 \approx 0.45$, and that $\bar{V}^{E}_{\max}$ grows with rising radius of the alkali ion (Figure 1).

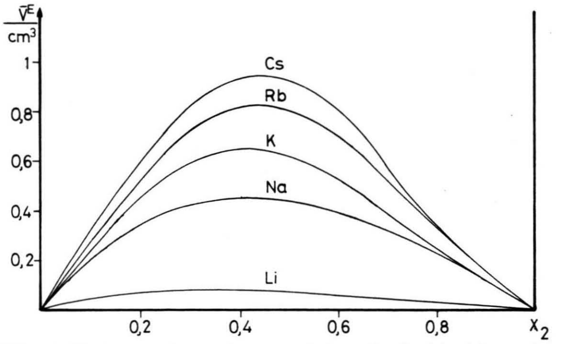

Fig. 1. Excess molar volumes of the alkali chloride + silver chloride mixtures at 1075 K.

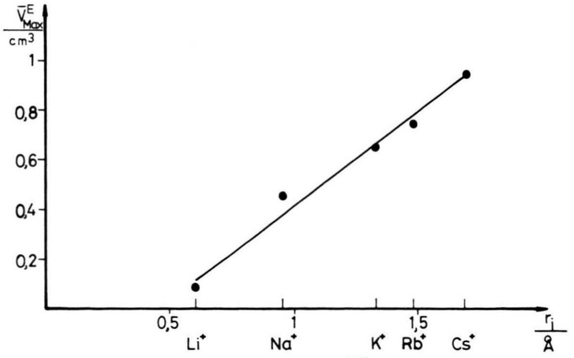

Fig. 2. The maximum values of $\bar{V}^{E}$ plotted against the radii of the respective alkali ions.

The plot of the maximum values against the radii of the alkali ions shows that there is a linear dependence (Figure 2).

The densities of molten salt mixtures are often estimatd from the densities of the pure components,

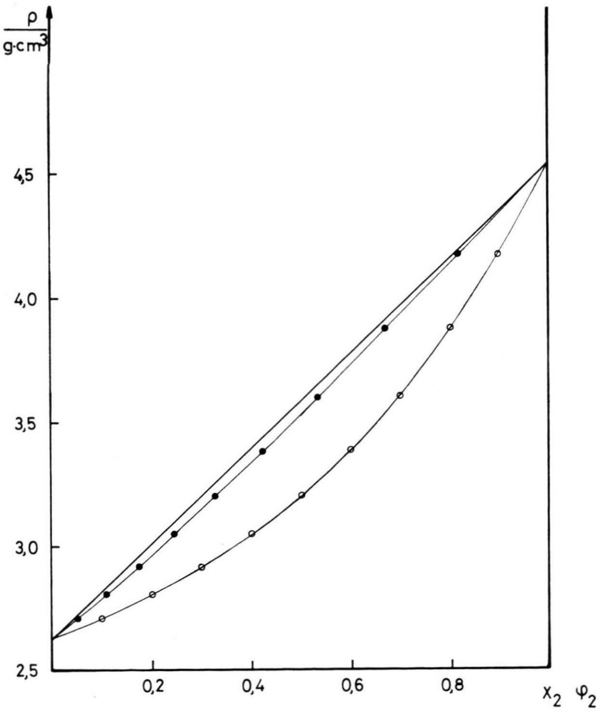

Fig. 3. The measured densities ϱ_m plotted against x_2 and φ_2 and the assumed ideal behaviour according to (5) and (6). System CsCl + AgCl at 1075 K. ● Density against the volume fraction, ○ Density against the mole fraction, — Ideal behavior of the density according to (5) and (6).

Table 2. Molar excess volumes of alkali chloride + silver chloride mixtures at 1075 K.

x_2	$\bar{V}^E/cm^3$				
	LiCl + AgCl	NaCl + AgCl	KCl + AgCl	RbCl + AgCl	CsCl + AgCl
0					
0	0	0	0	0	0
0.1	0.050	0.211	0.241	0.256	0.273
0.2	0.073	0.348	0.456	0.520	0.576
0.3	0.080	0.423	0.598	0.721	0.817
0.4	0.078	0.450	0.652	0.821	0.942
0.5	0.070	0.437	0.624	0.811	0.932
0.6	0.059	0.392	0.531	0.704	0.799
0.7	0.045	0.320	0.396	0.529	0.581
0.8	0.030	0.288	0.246	0.325	0.332
0.9	0.015	0.119	0.106	0.135	0.117
1	0	0	0	0	0

ϱ_1 and ϱ_2, according to

$$\varrho_m = x_1 \varrho_1 + x_2 \varrho_2 . \tag{5}$$

In the systems investigated here the maximum deviations from the measured densities are big: LiCl + AgCl: 1.2%, NaCl + AgCl: 5.2%, KCl + AgCl: 12.0%, RbCl + AgCl: 11.3%, and CsCl + AgCl: 10.7%. A much better estimation of ϱ_m can be done by assuming a linear relation with the volume fractions φ_1 and φ_2

$$\varrho_m = \varphi_1 \varrho_1 + \varphi_2 \varrho_2 \tag{6}$$

with

$$\varphi_2 = \frac{1}{\left(\frac{1}{x_2} - 1\right)\frac{M_1 \varrho_2}{M_2 \varrho_1} + 1} . \tag{7}$$

This assumption reduces the differences between estimated and measured densities by nearly one order of magnitude: LiCl + AgCl: 0.4%, NaCl + AgCl: 1.4%, KCl + AgCl: 1.4%, RbCl + AgCl: 1.9%, and CsCl + AgCl: 1.9% (Figure 3). Nevertheless the difference is still outside the sum of the experimental errors and the error due to the fit, which amounts to 0.3 – 0.5%.

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