A Physical Model of Molten Salt Data

Alexander Redkin, Yuri Zaikov, Olga Tkatcheva, and Anatoly Shurygin
Institute of High Temperature Electrochemistry, S. Kovalevskaya, 22, Yekaterinburg, 620219, Russia
Reprint requests to A. R.; E-mail: A.Redkin@ihte.uran.ru

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Molten alkali halides can be regarded as model ionic systems. Physical properties of molten alkali halides and their mixtures depending on molar volume and temperature are considered. The properties under examination are divided into two groups: cation-dependent and anion-dependent ones. The character of property changes with temperature and molar volume is different for these groups.

Key words: Molten Salts; Electrical Conductivity; Thermal Conductivity; Surface Tension; Molar Volume.

1. Introduction

The development of scientific research leads to fast increase of experimental data. In order to make proper use of their information a careful data analysis must be done. Molten salts are compounds formed by cations and anions. Consequently their properties are determined by the electronic structure of these ions depending on their element position in the periodic table. The first attempt to connect the place of elements in the periodic table and properties of molten salts was made by Biltz and Klemm [1]. They found the connection between the electrical conductivity of molten chlorides and the place of the respective cation in the periodic table. The chlorides of the 1 and 2 groups of elements possess the highest electrical conductivity. Almost one century of experimental investigation on molten salts has confirmed their supposition. The physical properties of salts cannot be directly derived from the electronic properties of the ions but it is possible to do this using the molar volume. The molar volume of salts depends on many factors: the size of the cations and anions, their charge, and their internal electronic structure. To characterize the ionic composition we chose the ionic potential \((Z_i e)/r_i\). Here, \(e\) is the electron charge, \(Z_i\) is the nominal charge of the cation, and \(r_i\) is its crystallochemical radius. For example, the dependence of a molten chloride’s molar volume on the ionic potential of the cation is presented in Figs. 1 and 2. The density data for calculating the molar volume were taken from Janz [2]. There are different trends in the molar volume formation for molten alkali chlorides and alkaline earth chlorides as well as rare earth chlorides. They allow to make a classification of molten salts according to their molar volume change with ionic potential and to divide them into several groups. In the frame of each group every property can be expressed via the molar volume by empirical equations. The role of the molar volume for molten salts is underestimated though maybe it plays the same role as the mean free path for gases and the shell parameter for solids because the molar volume reflects the basic electronic characteristics of cations and anions. A detailed analysis of some properties of molten salts and their mixtures, as far as it is volume-dependent, is the objective of this work.

2. Cation-Dependent Properties

Cations and anions have various influences on the physical properties mainly due to different sizes and charges. Cations have a relatively small extension and possess a higher mobility. Such property as the electrical conductivity is determined by cations. Viscosity reflects the resistance of a fluid to external forcing and the size of this resistance is mainly defined by those particles which have low mobility, i.e., by the anions. Let us consider how some cation-dependent properties change with the molar volume in alkali halides and their mixtures.
2.1. Electrical Conductivity

Alkali halides are the most ionic salts and possess high electrical conductivity ($\chi$) due to the low ionic potential of the alkali metal cations. Cations are the main electric charge carriers in molten salts. This resulted from transport investigations [3, 4]. Hence the electrical conductivity of salts and mixtures with common anion changes with the cation composition. That can be expressed via the molar volume ($V$). The dependence of the logarithm of the specific conductivity on the molar volume for molten halides is presented in Figure 3. The data for chlorides, bromides, and iodides are given for the temperature 1100 K [2]. There is a linear relationship between $\ln \chi$ and $1/V$ at constant temperature:

$$\ln \chi = K_1 + K_2/V.$$  

(1)

The coefficients $K_1$ and $K_2$ have reciprocal temperature dependence:

$$\ln \chi = A + B/T + (C + D/T)/V.$$  

(2)

This expression can be transformed into

$$\ln \chi = A + (B + D/V)/T + C/V;$$  

(3)

where the expression $(B + D/V)$ has the meaning of an activation energy. In exponential form (3) can be
written as
\[ \chi = A \cdot \exp[-(B - D/V)/T] \cdot \exp(C/V), \] (4)
where \( \chi \) is the specific conductivity in Ohm\(^{-1}\) cm\(^{-1}\), \( V \) is the molar volume in cm\(^3\)/mol, \( T \) is the temperature in K, \( A = \exp \tilde{A}, B = \exp \tilde{B}, C = \exp \tilde{C}, D = \exp \tilde{D} \) are empirical coefficients, listed in Table 1. This equation is valid for molten alkali halides and their ideal mixtures in the temperature interval 900 – 1200 K. For molten fluorides such dependence is slightly different [5] as an additional term \( \propto 1/V^2 \) contributes:
\[ \chi = A \cdot \exp[-(B - D/V)/T] \cdot \exp((C/V) + (E/V^2)). \] (5)

2.2. Thermal Conductivity

There is a relationship between the thermal conductivity \( \lambda \) of molten alkali halides and the inverse molar volume \( 1/V \) [6]. At constant temperature this reads as follows:
\[ \lambda = A + B/V. \] (6)
This equation can be rewritten into a temperature-dependent form. For molten alkali halides it is:
\[ \lambda = A + B/T + (C + D,T)/V, \] (7)
where \( \lambda \) is the thermal conductivity in W/(m K), \( T \) is the temperature in K. The empirical coefficients \( A, B, C, D \) for molten alkali fluorides and chlorides are listed in Table 2. These equations are valid for the temperature interval 1100 – 1250 K.

2.3. Relationship between Electrical and Thermal Conductivity

The electrical conductivity \( \chi \) as well as the thermal conductivity \( \lambda \) are cation-dependent properties. Therefore they can be inter-dependent as it is in metals (Wiedemann-Franz-Lorenz law). This relationship for molten alkali halides is also molar volume-dependent.
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Fig. 4. Relationship between the ratio of electrical and thermal conductivity for alkali halides at 1200 K versus molar volume.

Fig. 5. Dependence of the surface tension on the molar volume for KF-KCl, KF-KBr and KF-KI molten systems at 1200 K.

For molten alkali fluorides and chlorides it can be interpolated in the following form:

for fluorides:
$$\ln \frac{\chi}{\lambda} = -0.904 + \frac{2169}{T} + 0.029V,$$

for chlorides:
$$\ln \frac{\chi}{\lambda} = -5.78 - \frac{38881.9}{T} - 0.01865V. \quad (9)$$

3. Anion-Dependent Properties

Some properties are determined by larger size particles, i.e., by the anions. An example of such a property is the surface tension ($\sigma$). Anion-dependent properties decrease with the molar volume and temperature and they change with the anion composition. The dependence of the surface tension on the molar volume for potassium halide mixtures is presented in Figure 5. Experimental data for KF-KCl, KF-KBr and KF-KI molten salt systems at 1200 K are taken from the book of Stepanov [7]. At constant temperature the surface tension can be expressed in terms of the molar volume by

$$\sigma = A + \frac{B}{V}. \quad (10)$$

The coefficients $A$ and $B$ are temperature-dependent, so for potassium halide mixtures the volume-temperature...
dependence is:

$$\sigma = 43.9 - 0.69 T/V + 47.85/V - 0.0263 T.$$  \hspace{1cm} (11)

Here $\sigma$ is the surface tension in dyn/cm, $V$ is the molar volume in cm$^3$/mol, $T$ is the temperature in K. Equation (11) is valid in the temperature interval 1000–1200 K.

In mixtures with average anion surface tension ($\sigma$) this also changes linearly with the reciprocal molar volume, for example in the molten mixture LiF-KF. Data on this system are presented in Fig. 6 at the temperature 1200 K [7, 8]. The surface tension of this mixture in the temperature interval 900–1200 K is described by

$$\sigma = -23.66 - 0.0286 T + 2783.1/V + 84205.4/T.$$  \hspace{1cm} (12)

4. Conclusions

In molten salts and their mixtures all properties depend on either their cations or their anions. In the first case the respective property changes with the cation composition and the anion plays the role of a frame. In the second case the anion is the active participant of the process and the cation plays the role of a frame only. Thus every property can be presented in form of equations with temperature- and volume-dependent coefficients.