# Calculation of transport properties of cryolite melts

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The isotherm of viscosity and electrical conductivity of molten binary systems is calculated as a function of overheating. The proposed model of calculation is applied in the systems having sodium cryolite, $Na_3AlF_6$, as one component. It is shown that the proposed model describes the transport behaviour of the cryolite melts very well.

Concerning the viscosity, cryolite melts are interesting for several reasons. From the practical point of view the viscosity is one of the parameters characterizing the electrolyte used in the electrolytic production of aluminium. From the theoretical aspect the viscosity enables to judge upon the structural components of the electrolyte. This paper shows that the cryolite melts are also suitable for testing a model for calculating the viscosity of binary melts. There are two reasons for that. The viscosity of cryolite melts is determined mainly by the behaviour of large anions. The second reason is that the viscosity of these systems, *e.g.* $Na_3AlF_6-Li_3AlF_6$, considerably differs from additivity when it holds

$$C_{mix} = x_A C_A + x_B C_B, \qquad (1)$$

where $C_{mix}$ is the property of a mixture, $C_A$, $C_B$ are the properties of pure components, and $x_A$, $x_B$ are the mole and weight fractions of the respective components A and B in the mixture. (In the former case $C_{mix}$ is calculated per 1 mole of the mixture, in the latter case the specific property is calculated.)

Any model for calculation of the viscosity of molten salts is to explain these remarkable deviations from additivity.

In this work the viscosity is defined in the units of molar viscosity

$$Y = \frac{\eta}{\varrho} M = \eta V, \qquad (2)$$

where $Y$ is the molar viscosity, $\eta$ is the dynamic viscosity, $\varrho$ is the density, $M$ is the molar weight, and $V$ is the molar volume of the melt.

Using the molar viscosity for calculation of the viscosity of a mixture containing $n_A$ and $n_B$ moles of components A and B it follows that the viscosity defined in this way is the extensive quantity. Let us assume that the temperature dependence of the molar viscosity of pure substance may be expressed as

$$Y = Y^0 \exp E/RT, \qquad (3)$$

where $Y^0$ is the preexponentional factor, $E$ is the activation energy, $R$ is the gas constant, and $T$ is the absolute temperature.

Let us assume further that the viscosity of cryolite melts depends mainly on the behaviour of large anions $AlF_6^{3-}$ and $AlF_4^-$. Because the dissociation of $AlF_6^{3-}$ anion is approximately similar in $Na_3AlF_6$ and $Li_3AlF_6$ melts [1, 2] we can expect that the visco-

sity of the melts of the system $Na_3AlF_6-Li_3AlF_6$ will be only a function of overheating $\Delta T$ of the melt

$$\Delta T = T^f - T^c, \qquad (4)$$

where $\Delta T$ is the overheating of the melt, $T^f$ is the temperature of fusion of a pure component, and $T^c$ is the temperature of primary crystallization of the binary mixture. It has been found that the molar viscosity of a binary mixture $A-B$ can be expressed as the function of overheating in the following way

$$Y_{mix} = x_A\, Y_A^0\, \exp[E_A/R(T + k_A\, \Delta T_A)] + x_B\, Y_B^0\, \exp[E_B/R(T + k_B\, \Delta T_B)], \qquad (5)$$

where $k_A$ and $k_B$ are the constants which are to be determined from the experimentd It is assumed in this work that $k_A = k_B = k$. Thus the constant $k$ can be dete rmine. from one experimental measurement in the mixture $A-B$.
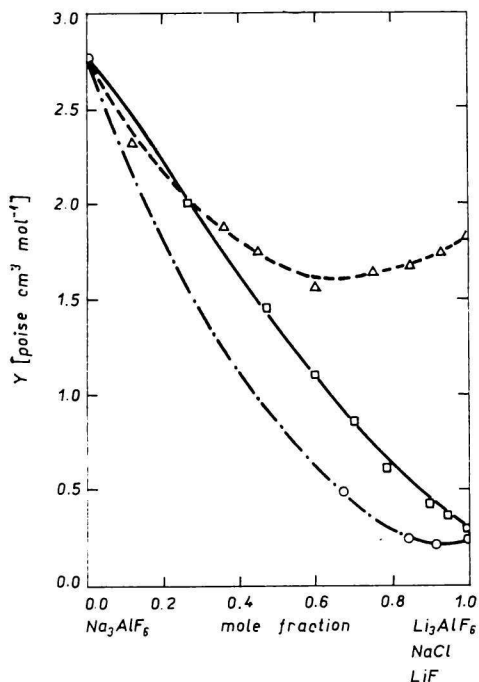


Fig. 1. Dependence of the molar viscosity on the composition at 1000°C.

$\lceil a_3AlF_6-Li_3AlF_6$: △ experimental va- .ues, − − − calculated according to eqn (5), $k = -0.40$;
$Na_3AlF_6-NaCl$: □ experimental values, ——— calculated according to eqn (5), $k = -0.25$;
$Na_3AlF_6-LiF$: ○ experimental values, −.−.− calculated according to eqn (5), $k = -1.10$.
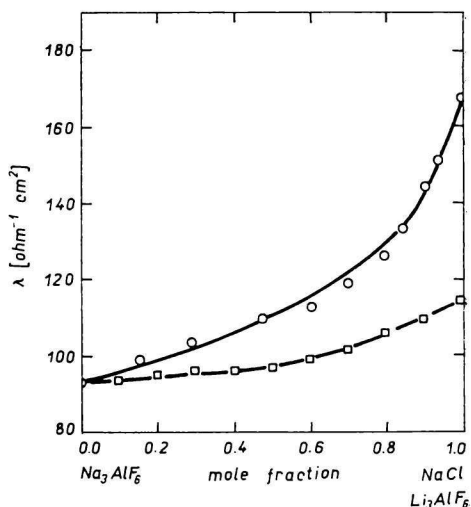
Fig. 2. Dependence of the equivalent electrical conductivity on the composition at 1000°C.

$Na_3AlF_6-LiAlF_6$: □ experimental values [4], − − − calculated according to eqn (5), $k = 0.39$;
$Na_3AlF_6-NaCl$: ○ experimental values [5, 6], ——— calculated according to eqn (5), $k = 1.75$.

The proposed method of calculation of viscosity was tested for three cryolite melts. The experimental data [3] and the data of molar viscosity of the mixtures $Na_3AlF_6-Li_3AlF_6$, $Na_3AlF_6-NaCl$, and $Na_3AlF_6-LiF$ calculated from eqn (5) are shown in Fig. 1 at temperature 1000°C. The agreement between calculated and experimental data is very good.

As it has been mentioned, the constant $k$ can be determined from one experimental value. Then this method of calculation can be used for the prediction of the course of viscosity in binary mixtures of molten salts. However, if we intend to use eqn (5) just for the description of experimental data we look for such a value of $k$ to obtain the best fitness between calculation and experiment. The physical background of the proposed model is supported also by the fact that eqn (5) can describe the dependence of viscosity on the composition even in the case when an inflection point appears on the curve as e.g. in the system $Na_3AlF_6-NaCl$. As can be expected, the absolute value of the factor $k$ decreases with increasing temperature. For example, the factor $k$ in the system $Na_3AlF_6-Li_3AlF_6$ achieves the value $-0.21$ at 1050°C, while it is $-0.40$ at 1000°C.

Eqn (5) was also used for calculation of the equivalent conductivity of the systems $Na_3AlF_6-Li_3AlF_6$ and $Na_3AlF_6-NaCl$ (Fig. 2). It is interesting that also in this case the agreement between experimental and calculated data is good. We cannot make here the same assumption as in the case of viscosity which is determined mainly by large ions. In the system $Na_3AlF_6-Li_3AlF_6$ the agreement between calculated and experimental data is very good. However, in the system $Na_3AlF_6-NaCl$ the relations are more complicated. From the study of the phase diagram of the system [7, 8] it can be assumed that the anion $Cl^-$ takes place in the formation of a complex ion with the aluminium and fluoride ions. It may explain why the calculated electrical conductivity has a simpler course than the experimental dependence even if the difference in absolute values is not too great.

From this work the following conclusions can be drawn:

The transport properties of binary mixtures of cryolite melts can be interpreted successfully as a function of overheating of the melt.

The proposed method of calculation enables one to predict the course of viscosity and electrical conductivity of binary mixtures of molten salts as the function of composition if only a few experimental data are known and even if there is a strong deviation of the dependence from additivity.

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