Relationship between Electrical Conductivity and Thermodynamic Properties of Binary Molten Salt Mixtures

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Electrical conductivity is a physical property reflecting the ability of a matter to transfer electrical charge. In molten salts conductance is due to ionic mobility which depends on many factors but the mostly the size of ions and ionic bond strength.
In order to consider the specific conductance change with the size of cation in systems with the same anion we can take reciprocal molar volume as an integral characteristic of the size. As one can see on fig 1 there is a straight line in coordinates ln χ- 1/V for molten halides at constant temperature, except fluorides.
For molten chlorides the expession is :

$$\ln\chi = 4{,}9^{*} \exp[-(2747-33724/V)/T] \ast \exp(53{,}7/V)$$

It means that integral cation mobility changes proportionally to reciprocal molar volume. This relationship is also valid for “ideal “ mixtures. In molten chlorides the system NaCl-KCl can be considered as a close to “ideal “ because Na^{+} and K^{+} have a very close electronic potential. Molar volume at mixing of molten NaCl and KCl is found to be additive [1] and the entalpy of mixing is very low[2].
As one can see from table 1 there is a good agreement between experimental values and those calculated .

Table 1. Comparison of experimental and calculated values for molten mixture NaCl-KCl at 1100 K

Molar fraction of NaCl	Experimental values $Ohm^{-1} \ast cm^{-1}$	Calculation on eq. 1 $Ohm^{-1} \ast cm^{-1}$
0,00	2,33	2,22
0,20	2,42	2,43
0,41	2,63	2,66
0,51	2,74	2,79
0,73	3,08	3,15
1,00	3,68	3,69

If the system is not “ideal” there is high entalpy of mixing and the deviations of molar volume and electrical conductivity from “ideal” behavior as one can see on the example of system CsCl-LaCl3 [3-5]

References

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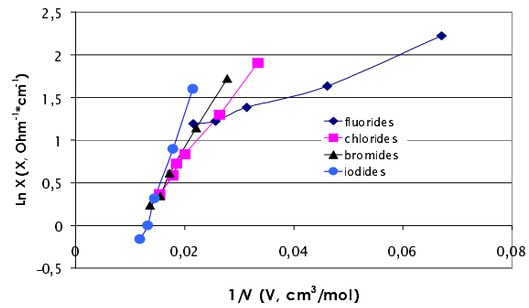

Fig. 1. Dependence of specific conductivity on reciprocal molar volume for molten fluorides (1270K), chlorides, bromides and iodides (1100K).

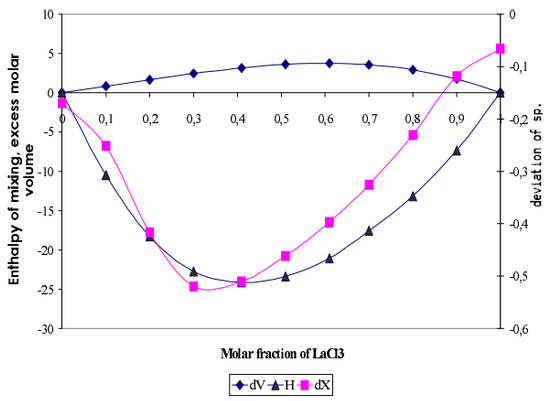

Fig.2 Deviation of specific conductivity [5]and molar volume[4] from “ideal “ values and concentration change of enthalpy of mixing[3]