

Introduction

Several characteristics of molten salts allow their utilization in many processes not possible with normal solvents. They are encountered as working fluids in various electro-mechanical and metallurgical processes such as metal and alloys production in molten salts bed, molten metal treatment, etc. Having an accurate knowledge of the transport properties of molten salts at high temperature is crucial for the efficient design of industrial equipments and chemical processes. Among these transport properties, viscosity is a key property not only in industrial applications but also to study the structure of liquids.

Because of the problems such as high temperature, high activity and corrosiveness, accurate measurements of properties such as viscosity are not simple tasks. Experimental data are limited and there are lots of discrepancy between them. Therefore, it is important to accumulate reliable experimental data and to establish predictive methods to forecast viscosity for situations where measured values are minimal and even nonexistent.

Methods

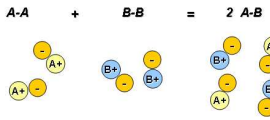
There are several theories to explain the mechanism of the momentum transport and estimate the viscosity of the liquids, where among them *Eyring's* theory provides a qualitative view of the momentum transport mechanism and permits rough estimation of the viscosity from other physical properties.

Simplified Eyring Eq.:

$$\eta = \frac{hN_{av}}{V_m} \cdot \exp\left(-\frac{G^*}{RT}\right) \quad (1)$$

Planck's constant h
Molar Viscous Activation Energy G^*
Molar Volume V_m Calculated by Density Model

Molar viscous activation energy (G^*) for pure salts has been considered as a linear function of Temperature (T). However, in multi component systems, the effect of composition should be also considered by taking into account the *interactions between different ion pairs* in the melt. Considering the following *quasi-chemical reaction* between second nearest neighbor pairs:



G^* for a multi component system, can be defined as a function of *pair fractions* (X_{ij}) and Temperature (T):

$$G^* = \sum X_{ij} \cdot G_{ij}^*$$

Equilibrium Pair Fractions
Calculated by Quasi-chemical Thermodynamic Model

$$G_{ij}^* = c_{ij} + d_{ij}T$$

Viscosity Model Parameters

For a 4-component system $NaCl-KCl-MgCl_2-CaCl_2$:

$$G^* = X_{AA}G_A^* + X_{BB}G_B^* + X_{CC}G_C^* + X_{DD}G_D^* + X_{AB}G_{AB}^* + X_{AC}G_{AC}^* + X_{AD}G_{AD}^* + X_{BC}G_{BC}^* + X_{BD}G_{BD}^* + X_{CD}G_{CD}^*$$

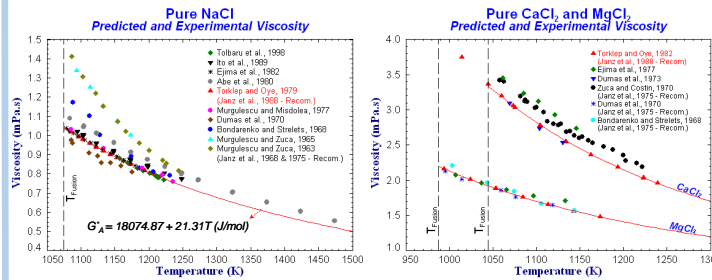
A: NaCl B: KCl C: MgCl₂ D: CaCl₂

To obtain model parameters:

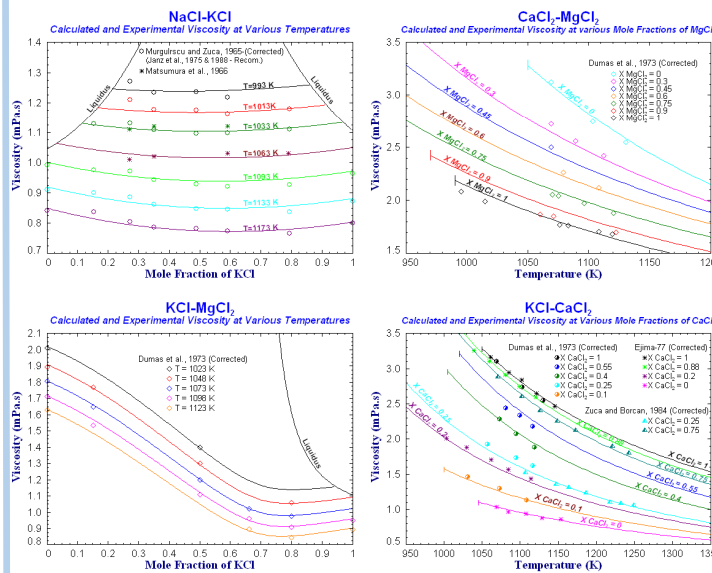
$$\ln(\eta \cdot V_m) = \ln(h \cdot N_{av}) + \frac{\sum X_{ij} (c_{ij} + d_{ij}T)}{RT}$$

$\ln(\eta \cdot V_m)$ versus $1/T$ is a straight line $\rightarrow c_{ij}, d_{ij}$

Step 1: Optimizing the Viscosity of Pure Molten Salts



Step 2: Optimizing the Viscosity of Binary Molten Salts



Step 3: Viscosity of Multi-Component Molten Salts

T (K)	Composition (Mol %)				EXP. η (mPa.s) Corrected	CALC. η (mPa.s)	Error (%)
	NaCl	KCl	MgCl ₂	CaCl ₂			
953	51.44	40.33	4.96	3.27	1.4790	1.4965	-1.2
973	51.44	40.33	4.96	3.27	1.4021	1.4020	0.0
993	51.44	40.33	4.96	3.27	1.3350	1.3164	1.4

Conclusions

The viscosity of industrially important $NaCl-KCl-MgCl_2-CaCl_2$ molten salt can be predicted by an Eyring's equation. The molar viscous activation energy (G^*) is extended as a function of *pair fractions* and temperature. In this approach to take into account the composition dependence of the viscosity, instead of using nominal mole fractions of the main salts, the equilibrium 2nd nearest-neighbor (cation-cation) pair fractions have been used. By simultaneously employing the thermodynamic model and density model, the presented viscosity model properly predicts the viscosity behavior of the studied molten salt systems in a fully consistent way.

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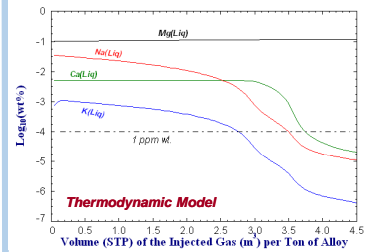
Application of the Model in Molten Aluminum Treatment Process

In order to meet the increasing demand of high quality aluminum, the quality of molten metal is a major concern of the aluminum industry. Therefore, it's crucial to remove undesirable impurities such as alkali metals.

1

In the following example, the removal of alkali metals by injection (at the bottom) of a mixture of $(Ar+Cl_2)_g + KMgCl_{3(s)}$ have been calculated.

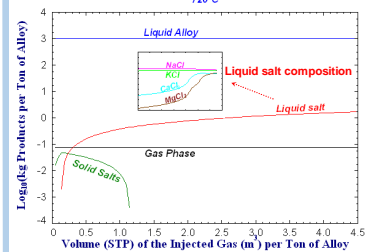
Alloy Composition



2

Cl_2 and $KMgCl_3$ react with alkali metals to form chlorides as solid particles or liquid droplets which will rise in the liquid alloy and continue to exchange alkali metal.

Reaction Products 720 °C



3

In this approach by combining fully consistent thermodynamic, density and viscosity models, the following properties of the molten salts are calculated.

Viscosity and Density of the Molten Salt

