VISCOSITY OF MOLTEN $NaF-AlF_3-Al_2O_3-CaF_2$ MIXTURES

Selecting and fitting models in a complex system

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A mathematical model has been developed to fit precision viscosity data for the range

$NaF-AlF_3$: $0 \leq x_{AlF_3}/(x_{NaF} + x_{AlF_3}) \leq 0.35$

$NaF-AlF_3$-4 wt% Al_2O_3: $0.05 \leq x_{AlF_3}/(x_{NaF} + x_{AlF_3}) \leq 0.35$

$NaF-AlF_3$-8 wt% Al_2O_3: $0.10 \leq x_{AlF_3}/(x_{NaF} + x_{AlF_3}) \leq 0.35$

$NaF-AlF_3$-12 wt% Al_2O_3: $0.20 \leq x_{AlF_3}/(x_{NaF} + x_{AlF_3}) \leq 0.30$

The experimentally observed Arrhenius temperature dependency and the Arrhenius mixing rule are retained in the model, with a modified Weibull distribution function substituted for the concentration terms. The 183 experimental data points were described with a 16 parameter model. The standard deviation was 0.58% which compares well with the experimental accuracy of the data. The development and pit-falls of modelling this complex system are discussed.

As an addendum a qualitative model for the effect of adding CaF_2 to some technological important $NaF-AlF_3-Al_2O_3$ mixtures is presented.

Introduction

An extensive experimental study on the viscosity of molten $NaF-AlF_3-Al_2O_3$ mixtures has recently been presented (1,2,3). The study covers the experimentally accessible range, limited by the solubility of Al_2O_3 and the total vapour pressure. The viscosity of 24 compositions was determined from the liquidus temperature up to 1100°C, representing a total of 183 experimental points.

A high-precision, computer-assisted viscometer developed at Institute of Inorganic Chemistry has been employed (4). Absolute viscosities are calculated from the damping of an oscillating cylinder using fixed photo-diodes. The results deviate significantly from previous data, being about 16% lower for cryolite (1)*).

The aim of the present paper is to give a unified treatment of the viscosity data for $NaF-AlF_3-Al_2O_3$ in terms of a mathematical model. Interpolation and extrapolation are easier with reference to a model, and a model is also expected to facilitate the use of the experimental data in a hydrodynamical type model connected to the electrolytic production of aluminium. The primary goal has been to represent the system with a minimum of parameters giving an accuracy comparable to the experimental data without introduction of artifacts.

The effect on the viscosity of adding CaF_2 to some selected melts is discussed in an addendum.

Model fit program

The employed program for fitting the viscosity data to mathematical models is a general purpose nonlinear regression program, MODTLP (6). Emphasis is put upon flexibility and ease in use.

The general model structure accepted by the program is formulated as

$$Y_{i,j,k} = F_j(\underline{\theta}, \underline{x}_i, \underline{t}_{ik}) + \varepsilon_{ijk} \qquad (1)$$

where

- i = 1,2,...AR : number of experimental runs
- j = 1,2,...M : number of simultaneous responses
- k = 1,2,...N(i) : number of observations for run i
- $\underline{\theta}$ = vector of NP model parameters, P of which can be adjusted by the calculations
- $\underline{x}_i$ = vector of K independent variables constant for run i
- $\underline{t}_{ik}$ = vector of L independent variables for observation k in run i
- $\underline{\varepsilon}_{ijk}$ = experimental error.

The functional relations may be given explicity, or implicity as by solution of a set of nonlinear equations or integration of a set of differential equations.

Six different criteria for the fit are developed from the maximum likelihood principle and the user chooses the one corresponding to the statistical structure of his experimental data.

The criterion is minimized by a simplex algorithm as given by Nelder and Mead (7). This routine is very robust and insensitive to poor initial estimates of the parameters. It suffers from the slow convergence behaviour which characterize the direct search minimization algorithms. To counteract this, a strategy is developed which uses a rough convergence criterion for the simplex minimization. Then a second order surface is fitted to the simp-

*) New values for NaCl recommended to U.S. National Bureau of Standards deviate up to -30% from previous recommendation (4,5).

lex points and an improved estimate of the minimum is calculated analytically.

The standard deviation of the single parameters, their correlation matrix and their eigenvalues are important diagnostic information used to judge the significance of the parameters and the adequacy of the model. A graphical package is used to produce a graphical representation of the results.

One great advantage of this program is the opportunity to specify that a subset of the defined parameters is to be adjusted during the calculations and that the remaining ones are kept constant at their initially given value. This allows a very general model formulation for a given problem and to proceed in a stepwise development of the significant parts of the model with no reprogramming and little change of the input data.

Models for the temperature variation

An Arrhenius type description of the temperature dependency of molten salt viscosities has been found to be superior to a polynomial expression, with respect to the number of adjustable parameters and reliability in extrapolation.

A simple Arrhenius dependency

$$\ln\eta = a + b/T \qquad (2)$$

where T is the Kelvin temperature describes, for instance, the viscosity of NaF over a 100°C temperature interval with a 0.03% standard deviation (1).

Deviations from Equation (2), which may occur in more complex liquids, are usually well described by a second-order term, giving

$$\ln\eta = a + b/T + c/T^2. \qquad (3)$$

The use of the straightforward Equations (2) and (3) have, however, the disadvantage that the parameters a, b and c are strongly correlated, leading to corresponding convergence problems in the actual parameter estimation.

If the simple relationship of Equation (2) is valid it is recommended to use the equation

$$\eta = A\exp[B(1/T-1/T_m)] \qquad (4)$$

where T_m is chosen as an arbitrary mean temperature.

Otherwise, it is useful to express the relationship so that the second-order term is (nearly) orthogonal and thus a measure of the curvature. This is obtained by introducing an additional arbitrary temperature T_u. If the deviation from linearity appears in the low temperature range, T_u is given a round value within the high-temperature linear region, *e.g.* the approximate maximum temperature. In the opposite case, a low temperature is chosen. If the deviation occurs in both ends of the temperature interval, then $T_u = T_m$.

The resulting equation is

$$\eta = A\exp[B(1/T-1/T_m)+C((1000/T-1000/T_u)^2-(1000/T_m-1000/T_u)^2)]. \qquad (5)$$

The parameters A, B and C are much less correlated than a, b and c, and numerical problems in the modelfitting are minimized. This re-parameterization was originally suggested by Box (8). The resulting viscosity equations for the 24 $NaF-AlF_3-Al_2O_3$ mixtures are given in Ref. (1), Table 1, and Ref. (2), Table 4.

Physically-based models

The viscosity of liquid mixtures of $NaF-AlF_3-Al_2O_3$ shows a complex dependency on composition, see for instance Fig. 4, reflecting the structural complexity of these melts. In the binary $NaF-AlF_3$ system the anions F^-, AlF_6^{3-} and AlF_4^- are generally recognized, while a series of Al-O-F containing species have been suggested in the ternary $NaF-AlF_3-Al_2O_3$ system.

For binary complex-forming systems such as $NaF-AlF_3$ and $NaAlCl_4-AlCl_3$ we have been able to describe the viscosities with the following equations (1,2,3,9):

$$\ln\eta_i = \alpha_i + \beta_i/T \qquad (6)$$

$$\ln\eta = \sum_i x_i \ln\eta_i + E \qquad (7)$$

where η_i is the viscosity of each anionic or molecular species i, η the viscosity of the mixture and x_i the mol fraction of species i in the mixture. The constants α_i and β_i are adjustable parameters. An interaction parameter E is sometimes added. Physically, this set of equations assumes the existence of additive, temperature-independent activation energies of viscous flow.

A species model has the advantage that the parameters have a straightforward physico-chemical interpretation and may be known *a priori* from previous studies permitting direct comparison. A disadvantage is that the viscosity is given an implicit form through non-linear equilibrium equations.

Many-species models for the present ternary system with structural units F^-, AlF_6^{3-}, AlF_4^- and two additional oxygen-containing species were attempted. The following pairs of oxygen species were chosen: $Al_2O_2F_4^{2-}$-$Al_2OF_6^{2-}$, $AlOF_3^{2-}$-$Al_2OF_6^{4-}$, $Al_2O_2F_6^{4-}$-$Al_2OF_6^{2-}$. However, the models failed to describe the data even in a qualitative way.

A model with more than 2 oxygen-containing species may have succeeded, but it was decided not to pursue the species concept further for this system. The most serious argument against further elaboration of the species model is simply that the structure of the oxygen-containing species has not been established with any certainty, despite numerous studies (10). The structure of this melt system may also possibly better be described by network formation, especially at high Al_2O_3 concentrations. The mathematical inconvenience also becomes rather formidable with 6 and 7 species models, and the results may have little or no relation to structural realities.

Mathematical experimental-related models

Further modelling were performed in two stages. The first model made use of the experimentally observed Arrhenius temperature dependence and the Arrhenius mixing rule, but the bothersome determination of species concentrations through equilibrium equations was avoided by using polynomials. The second and most successful model retained the Arrhenius concept, but the polynomials were replaced with mathematical functions which had functional forms similar to the observed concentration dependence.

The construction of weight-functions for the concentration terms n_i constituted the main problem in the first model. The following functions were finally chosen:

$$\ln\eta = \sum_{i=1}^{m} n_i \ln\eta_i + \sum_{i=1}^{m-1} \sum_{j=i+1}^{m} n_i n_j \kappa_{ij} \qquad (8)$$

$$\ln\eta_i = \alpha_i + \beta_i(1/T-1/T_m)$$

$$n_i = a_i + b_i x + c_i y + d_i xy$$

$$\kappa_{ij} = \kappa_{ij}^{o}\exp(E_{ij}(1/T-1/T_m)$$

where

$m = 3$

$x = 100x_{AlF_3}/(x_{NaF}+x_{AlF_3})$

y = weight percent Al_2O_3

T = temperature in K

η_i = hypothetical viscosity of component i (temperature function only)

E_{ij} = interaction parameter.

This model gives 24 adjustable parameters. The best result obtained with the model is illustrated in Figure 1. The figure shows clearly that the three-term model fails to describe the isotherms of the binary system and of the melts with low Al_2O_3 content. The temperature description was not any better and the overall relative standard deviation for the fit was 5.0%.

In the second type of model the polynomial form of the concentration term was abolished and several candidate functions were considered which could describe more effectively the viscosity *versus* composition. The Weibull distribution function in the form

$$f(p) = a\cdot b(d-p)^{a-1}\exp\left(b(d-p)^{a}\right) \qquad (9)$$

was finally chosen. Here p could be either x or y and the parameters a, b, and d functions of T and the one of x or y not included in p.

This function is very flexible and can describe the skewed bellshaped form shown in the x-variation of the viscosity data (Figures 4-6).

The Weibull function based model was arrived at in a stepwise fashion described below. The complete model had the form:

$$\begin{aligned}\ln\eta = {} & (1-(x/100))\ln\eta_{NaF} \\ & + xb_y(d_y-x)\exp(-b_y(d_y-x)^2)\exp(-c_y y/(x+1))[\alpha_x+\beta_x(1/T-1/T_m)] \\ & + yb_x(d_x-y)\exp(-b_x(d_x-y)^2)\exp(-c_x x)[\alpha_y+\beta_y(1/T-1/T_m)] \\ & + (x/(x^2+100))\exp(-e_1(25-x)^2)\exp(-e_2y^2)[\alpha_z+\beta_z(1/T-1/T_m)] \qquad (10)\end{aligned}$$

where

$x = 100x_{AlF_3}/(x_{NaF}+x_{AlF_3})$ and y: weight% Al_2O_3

$b_p = (b_{po}+b_{p1}\cdot p)\exp(b_{p2}(1/T-1/T_m))$ $\quad p = x,y$

$d_p = (d_{po}+d_{p1}\cdot p)\exp(d_{p2}(1/T-1/T_m))$ $\quad p = x,y$

$c_p = c_{po}\exp(c_{p2}(1/T-1/T_m))$ $\quad p = x,y$

η_{NaF} = measured viscosity of NaF

(24 parameters)

In this model the Arrhenius temperature dependence and the Arrhenius mixing rule are still retained. The contribution from NaF is given as the first term. The second term was first used to describe the variation of viscosity with no Al_2O_3 present. When Al_2O_3 was present a third term was added and the second and third term multiplied with an exponential term containing the concentration parameter not included in the first exponential. The form $y/(x+1)$ of the exponent in the last part of the second term was chosen in order to give the strongest increase in viscosity with Al_2O_3-addition for low contents of AlF_3. Initially the fourth term was not included, but it was introduced to perform corrections around x = 25, *i.e.*, around the maximum. The general strategy of model building is hence not to use general functions, for instance a polyno-

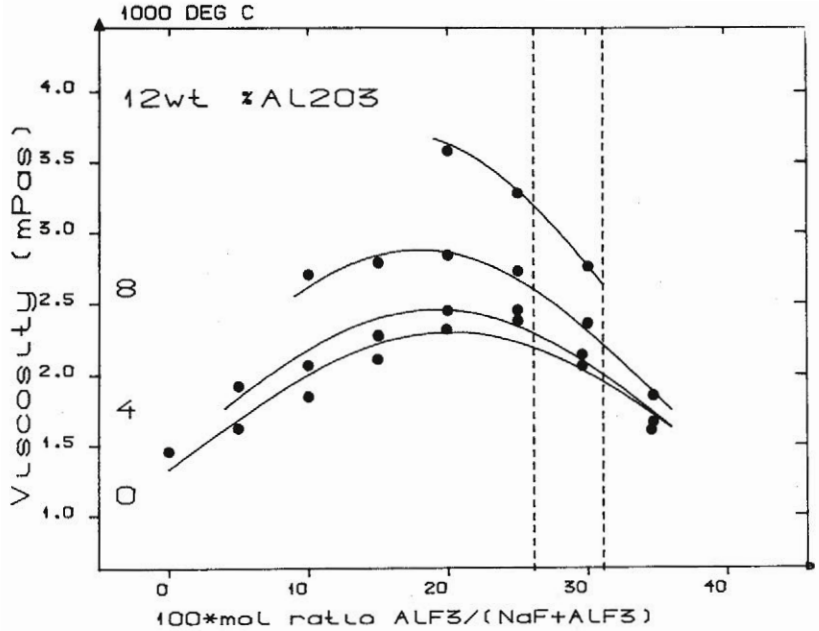

Fig. 1. Experimental NaF-AlF_3-Al_2O_3 viscosities at 1000°C compared with a polynomial model (Equation 8).

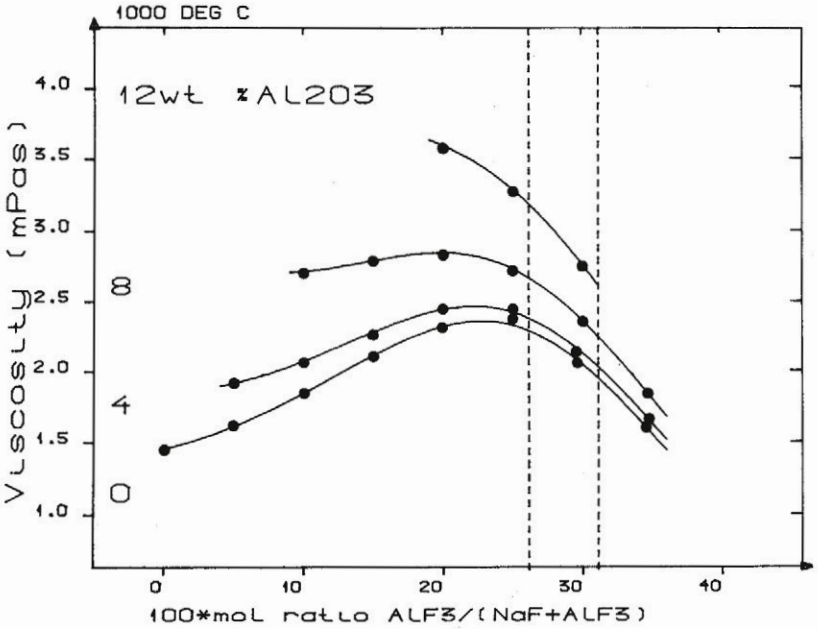

Fig. 2. Experimental NaF-AlF_3-Al_2O_3 viscosities at 1000°C compared with a 3-term modified Weibull-function model (Equation (10) without last term).

mial, but a step-by-step introduction of functions that have been critically examined for effectiveness in describing the experimental observations with a minimum of parameters.

The final model was developed from Equation (10) as follows. The two first terms of Equation (10) with y=0 were used to describe the binary $NaF-AlF_3$ system. The 6 adjustable parameters were fitted to the experimental data for the 8 binary $NaF-AlF_3$ mixtures. The parameter b_{y2} was not statistically significant and set to zero. The resulting 5 parameter description of the binary system gives a standard deviation of 0.58%, and is represented by the lowest curve in Figure 2.

The 5 parameters in the second term of Equation (10) were kept unchanged when the third term was added for the ternary system. Both terms were given multiplicative crossterms which cancel for x or y = 0. In the first attempt to fit the complete set of data, linear x and y variations of the b_p and d_p parameters were neglected giving 10 additional parameters.

The parameters c_{y2} and b_{x2} were not significant and set to zero. This gave a total of 13 adjustable parameters and came out with a standard deviation of the fit of 0.73%. The result is illustrated in Figure 2. An examination of the deviation between experimental and calculated viscosities showed that the model did not give an adequate description for low contents of Al_2O_3 and $0.20 \leq x_{AlF_3} \leq 0.30$. The last term in Equation (10) was now introduced to correct the two lowest curves of Figure 2 around their maxima. Four new parameters were introduced through this addition, while the previous parameters were kept constant, in the first trial. Total estimation of all 17 parameters gave a relative standard deviation of 0.56%. The result is given in Figure 3.

Figure 3 is a very clear demonstration of the pitfalls of model building. Although the complete Equation (10) has a moderate number of parameters relative to the experimental material (183 observations), the last term has become too specific to the composition x = 25 where the measuring density is not higher than anywhere else (measurements at each 5 mol%).

This was corrected in the final fit by choosing a fixed and lower value of e_1. In this fit we also let all 23 parameters (except e_1) in Equation (10) vary in a significance test. The same 17 (16 adjustable) parameters remained whose values and standard deviations are given in Table I.

The reduced final equation for the viscosity of the $NaF-AlF_3-Al_2O_3$ system is then summarized as

$$\ln\eta = (1-(x/100))\ln\eta_{NaF} + x(d_y-x)[\exp(-b_y(d_y-x)^2)][\exp(-c_y y/(x+1))]\ln\eta_x + y(d_x-y)[\exp(-b_x(d_x-y)^2)][\exp(-c_x x)]\ln\eta_y + (x/(x^2+100))[\exp(-e_1(25-x)^2)][\exp(-e_2 y^2)]\ln\eta_z \quad (11)$$

where

$x = 100x_{AlF_3}/(x_{NaF}+x_{AlF_3})$ and y: weight% Al_2O_3

$t = 1/T-1/1273.15$

$\ln\eta_{NaF} = 0.37758+3184t$ (experimental)

$\ln\eta_x = 0.001934+10.99t$

$\ln\eta_y = 0.01502+47.22t \quad b_y = 8.515\cdot10^{-4}$

$\ln\eta_z = 1.188+5300t \quad c_y = 0.6111$

$d_y = 37.89\exp(619.3t) \quad b_x = 0.002657$

$d_x = 30.12\exp(-508.9t) \quad e_1 = 0.05$ (chosen)

$c_x = 0.04051\exp(1948t) \quad e_2 = 0.02253$

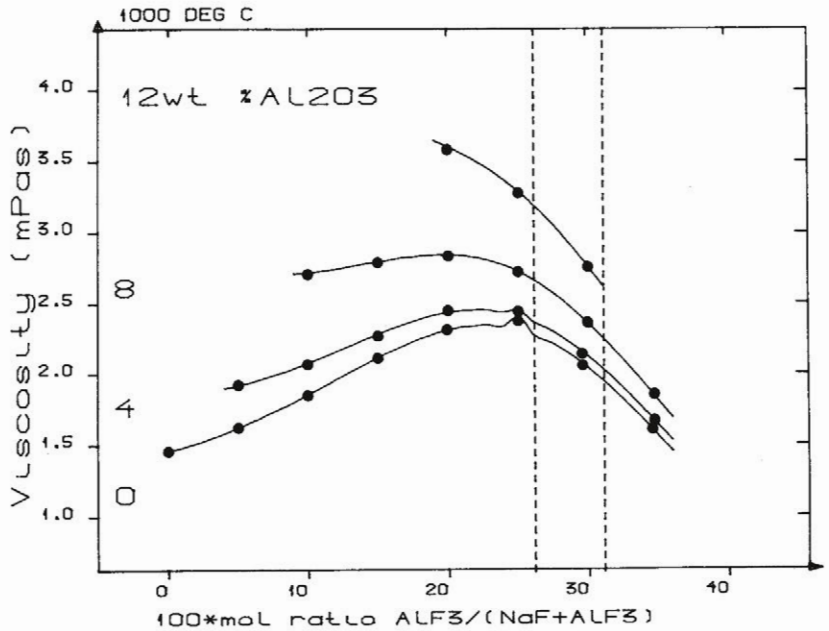

Fig. 3. Experimental $NaF-AlF_3-Al_2O_3$ viscosities at 1000°C compared with a modified Weibull-function model (Equation (10) but without restriction on e_1). Note improbable functional form around x = 25.

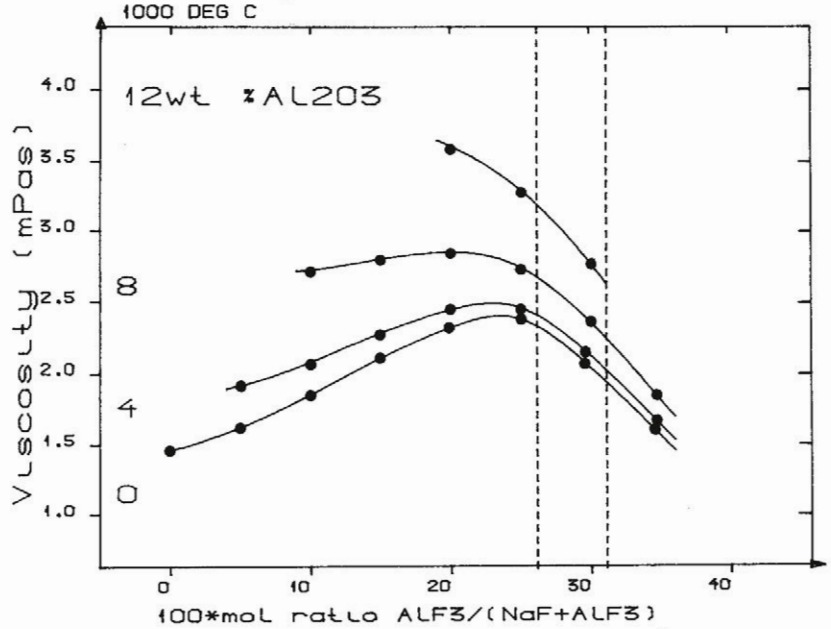

Fig. 4. Experimental $NaF-AlF_3-Al_2O_3$ viscosities at 1000°C compared with a modified and restricted Weibull-function model (Equation (11)).

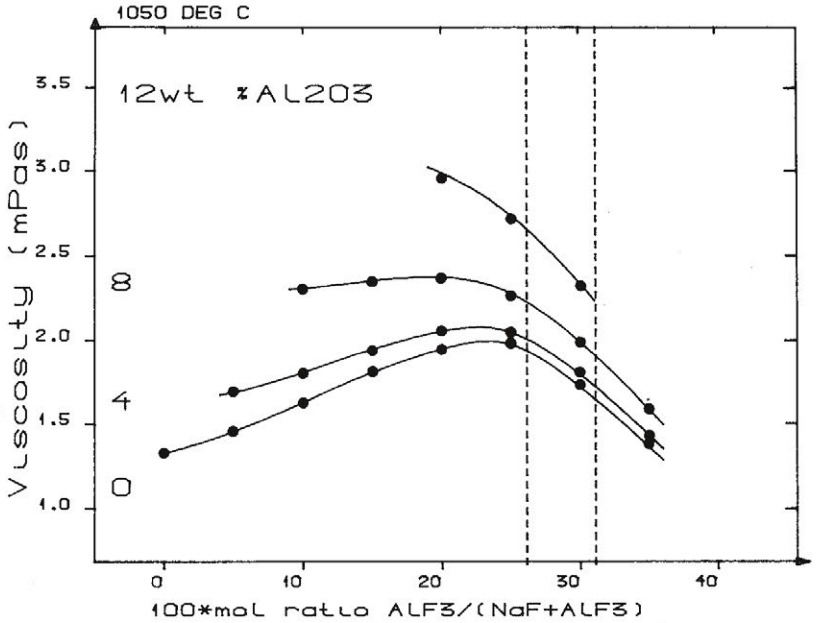

Fig. 5. Experimental NaF-AlF_3-Al_2O_3 viscosities at 1050°C compared with a modified and restricted Weibull-function model (Equation (11)).

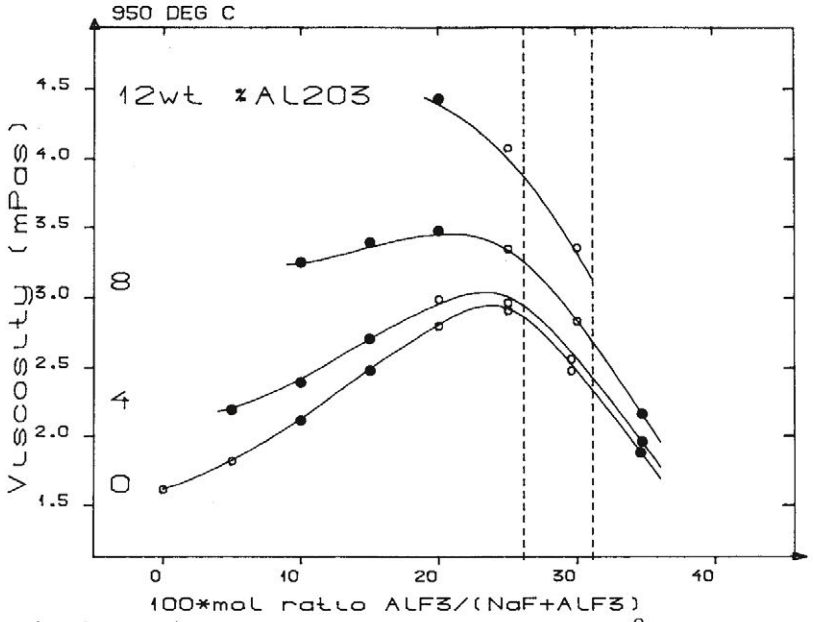

Fig. 6. Experimental NaF-$AlF_3Al_2O_3$ viscosities at 950°C compared with a modified and restricted Weibull-function model (Equation (11)). Values extrapolated more than 10°C are given as open circles.

Table I. Parameters in Equation (11) and their standard deviations

Parameter	Estimated value	Estimated standard deviation
α_x	$1.934 \cdot 10^{-3}$	$2.1 \cdot 10^{-5}$
β_x	10.99	0.25
α_y	$1.502 \cdot 10^{-2}$	$3.2 \cdot 10^{-4}$
β_y	47.22	5.6
α_z	1.188	0.16
β_z	5 300	3 300
b_y	$8.515 \cdot 10^{-4}$	$1.8 \cdot 10^{-5}$
b_x	$2.657 \cdot 10^{-3}$	$2.0 \cdot 10^{-4}$
c_y	0.611	0.039
c_{xo}	$4.051 \cdot 10^{-2}$	$4.6 \cdot 10^{-4}$
c_{x2}	1 948	316
d_{yo}	37.89	0.052
d_{y2}	619.3	24
d_{xo}	30.12	1.1
d_{x2}	-508.9	132
e_1	$5 \cdot 10^{-2}$	chosen
e_2	$2.253 \cdot 10^{-2}$	$5.2 \cdot 10^{-3}$

Table II. Comparison of experimental results and model, Equation (11).

Composition given as x-y	Number of exp. points (mean values)	Temp. interval °C	Standard deviation in temperature fit, %	Standard deviation in discrepancy from model %
0-0	6	1000-1100	0.03	0.07
5-0	6	1000-1100	0.10	0.51
10-0	7	950-1100	0.10	0.30
15-0	7	950-1100	0.09	0.27
20-0	6	1000-1100	0.13	0.13
25-0	5	1015-1114	0.17	0.32
30-0	8	997-1059	0.75	0.88
35-0	8	951-1041	0.71	0.85
5-4	7	982-1100	0.13	0.45
10-4	9	941-1099	0.17	0.68
15-4	13	920-1100	0.13	0.43
20-4	9	970-1101	0.07	0.40
25-4	7	990-1102	0.27	0.42
30-4	6	981-1084	0.48	0.83
35-4	7	919-1040	0.22	0.73
10-8	8	940-1080	0.05	0.41
15-8	9	936-1101	0.08	0.72
20-8	7	959-1081	0.31	0.50
25-8	7	980-1101	0.08	0.31
30-8	7	970-1082	0.48	0.73
35-8	9	900-1041	0.64	0.56
20-12	9	958-1100	0.12	0.66
25-12	8	970-1101	0.44	0.87
30-12	8	998-1094	0.43	0.55

Equation (11) contains 16 adjustable parameters. The standard deviation of the viscosity in the fit was 0.58%.

The equation is considered valid over the entire liquid range up to x = 35 and t = 1100°C.*)

The overall standard deviation of 0.58% compares well with the experimental uncertainty of the individual data points, given in Table II as the standard deviation in the viscosity *versus* temperature fits for each melt (Equations (2) or (5)). The experimental scatter is highest in AlF_3-rich mixtures, mainly for reasons connected with increased evaporation. These are also the melts whose experimental viscosities deviate the most from the values predicted by the model (Table II, column 5).

Compared with the excellent agreement at 1000°C and 1050°C, Figures 4 and 5, the extrapolated data in Figure 6 show some deviation from the curves calculated from the model. Again, this is according to expectations since only data points within the experimental temperature range were used in fitting the model.

Addition of CaF_2 to NaF-AlF_3-Al_2O_3 melts

The aim in adding CaF_2 to NaF-AlF_3-Al_2O_3 melts was to describe the influence of CaF_2 on the viscosity of technical melts. Four quaternary mixtures, all with 5 wt% CaF_2, were measured. The complete set of experimental data will be given elsewhere, but in Table III we have visualized the influence of CaF_2 through a few comparisons. The data may need to be adjusted up to 1-2 absolute % if more reliable density data (required in computing the viscosity) become available.

A quantitative model describing the influence of CaF_2 has not yet been developed, but a qualitative model emerges from the results in Table III.

Table III. Percentage increase in viscosity by adding CaF_2.

Nominal composition* before addition of CaF_2	Viscosity increase at 5 wt% CaF_2 (%) 1000°C	1100°C
25 - 0	6.6	6.2
25 - 8	5.6	5.3
30 - 0	10.4	7.6
30 - 8	12.7	8.7

*100·mol ratio $AlF_3/(NaF+AlF_3)$ - wt% Al_2O_3.

The influence of CaF_2 can be separated into a cationic and an anionic part:

1) The addition of Ca^{2+} ions will increase the viscosity.
2) The addition of CaF_2 is equivalent to $2F^-$ from NaF and will shift the composition to an apparent lower $AlF_3/(NaF+AlF_3)$ ratio with a resulting increase in viscosity for the present mixtures.

The resulting apparent x'_{AlF_3} is given from stoichiometry as:

$$x'_{AlF_3} = \frac{x^o_{AlF_3}}{1 + \dfrac{2z(x^o_{NaF}M_{NaF} + x^o_{AlF_3}M_{AlF_3})}{(1-z)(1-y^o)M_{CaF_2}}} \qquad (12)$$

where x denotes mol fraction, M molecular weight, y and z wt fraction of Al_2O_3 and CaF_2 and the superscript ^{o} gives values before addition of CaF_2.

With reference to Figures 4-6 the above model explains why the influence of CaF_2 is more pronounced for mixtures with $x^o_{AlF_3} = 0.30$ than for $x^o_{AlF_3} = 0.25$, and why the influence of CaF_2 diminishes with increasing temperature. In a rough way addition to 5 wt% CaF_2 at 1000°C is estimated to give an increase of about 3% due to Ca^{2+}, while a shift of the $AlF_3/(NaF+AlF_3)$ ratio of about 0.025 is responsible for the remaining viscosity increase.

*) Users of Equation (11) might check their calculations against this example: T=1273.15 K, x=30 (mol ratio NaF/AlF_3=2.33), y=8 weight% Al_2O_3, calculated viscosity = 2.345 mPas (or centipoise).

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