

# Fusibility and structure of the NaF-rich melts in the NaF—NaAlSi<sub>3</sub>O<sub>8</sub> and NaF—KAlSi<sub>3</sub>O<sub>8</sub> systems

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*Dedicated to Professor E. Treindl, DrSc., in honour of his 60th birthday*

The liquidus curves of NaF in the NaF—NaAlSi<sub>3</sub>O<sub>8</sub> and NaF—KAlSi<sub>3</sub>O<sub>8</sub> systems were determined using the thermal analysis and the visual thermal analysis methods. Different courses of the liquidus curves were found depending on the nature of the system under investigation. Various thermodynamic approaches were applied for the NaF activity calculation. The best fit of the experimental and calculated values of the temperature of primary crystallization of NaF was obtained if neither a chemical reaction between the fluoride anions and the feldspar polyanions nor a full disintegration of the feldspar anions were considered. In the NaF—NaAlSi<sub>3</sub>O<sub>8</sub> system, the interaction energy of 21 kJ mol<sup>-1</sup> is probably necessary for the exchange reaction of the accompanying calcium oxide (as impurity) with sodium fluoride. In the NaF—KAlSi<sub>3</sub>O<sub>8</sub> reciprocal system, the standard Gibbs energy of the exchange reaction was included in the calculation.

Кривые ликвидуса NaF в системах NaF—NaAlSi<sub>3</sub>O<sub>8</sub> и NaF—KAlSi<sub>3</sub>O<sub>8</sub> были определены с применением методов термического и визуального термического анализов. Обнаружено, что различия в ходе кривых ликвидуса зависят от природы исследуемых систем. Различные термодинамические подходы были использованы для расчета активности NaF. Наилучшее совпадение экспериментальных и рассчитанных значений температуры первичной кристаллизации NaF было получено, если не учитывалась химическая реакция между фторидными анионами и полевошпатовыми полианионами, ни полная дезинтеграция полевошпатовых анионов. В системе NaF—NaAlSi<sub>3</sub>O<sub>8</sub> вероятно необходима энергия взаимодействия порядка 21 кДж моль<sup>-1</sup> для протекания обменной реакции между примесной окисью кальция (в качестве загрязнения) и фторидом натрия. В равновесной системе NaF—KAlSi<sub>3</sub>O<sub>8</sub> стандартная энергия Гиббса обменной реакции была учтена при расчете.

The study of the NaF—feldspar system has a particular importance as it may be used as electrolyte for the electrodeposition of aluminium—silicon alloys from natural minerals dissolved in molten salts [1]. Sodium and/or potassium

feldspars seem to be the most interesting minerals because of their wide occurrence in several regions of Norway. The relatively good solubility of various types of natural feldspars in molten fluorides is the decisive factor for choosing NaF as the solvent.

Besides the practical utilization, the NaF—feldspar melts are also interesting from the theoretical point of view as they represent liquids containing two different kinds of ionic compounds: the classical ionic NaF and the aluminosilicate network forming feldspar which, naturally, also belongs to the ionic liquids. By mixing these different kinds of liquids several types of interactions are possible which may substantially affect the structure of the melt and consequently also its physicochemical properties, including the activity of the components. The attention was focused on the NaF-rich section of the investigated systems which are interesting with respect to the potential utilization.

For the theoretical analysis of the NaF liquidus curves, the fundamental question is the behaviour of the polymerized feldspar anions in the dilute solution of feldspar in NaF. Three possible situations may occur:

i) The feldspar anions are fully dissociated to separate ions or new complex ions.

ii) Only some of the Si—O—Si or Al—O—Si bonds break due to the fluoride anions and consequently the polymerization degree of the feldspar anions is reduced.

iii) The integrity of the feldspar anions,  $(\text{AlSi}_3\text{O}_8)_n^-$ , does not change.

The effect of the addition of fluorides on the structure of liquid silicates has been investigated by several authors. *Kozakevitch* [2] studied the effect of calcium fluoride on the viscosity in the system  $\text{CaO—Al}_2\text{O}_3\text{—SiO}_2$ . Additional study of the same topic has been carried out by *Bills* [3]. On the basis of the experimental results it was postulated that fluoride ions do not replace oxygen ions in the aluminosilicate anions. This is consistent with the fact that no new compounds were found in the respective phase diagrams which would be the case if the substitution of fluoride ion for an oxygen one took place in the silicate network. It was thus suggested by *Bills* [3] that the calcium fluoride acts as a solvating agent for the large silicate anions.

*Shartsis et al.* [4] measured viscosities in the alkali silicate systems. They found that the viscosity decreases in the order K, Na, Li, which is the reverse of the order expected on the basis of the cation—oxygen ion bond strength. This indicates that the possible factor affecting the viscosity is the size of the alkali cation because the electrostatic binding of silicate anions depends on the field strength of cations.

In the present work the liquidus curves of NaF in the NaF— $\text{NaAlSi}_3\text{O}_8$  and NaF— $\text{KAlSi}_3\text{O}_8$  systems were determined experimentally. The experimental

results were compared with the liquidus curves calculated for the three possible behavioural patterns of the feldspar anions mentioned above.

### Experimental

For the preparation of samples, carefully selected crystals of natural sodium feldspar,  $(\text{Na}_{0.86}, \text{Ca}_{0.14})\text{Al}_{1.14}\text{Si}_{2.86}\text{O}_8$ , and potassium feldspar,  $(\text{K}_{0.81}, \text{Na}_{0.19})\text{AlSi}_3\text{O}_8$ , from Glams-lad, Norway and anal. grade NaF were used. For simplicity both feldspars were considered as pure components regardless of the relatively high content of accompanying calcium and sodium oxides.

The temperature of the primary crystallization was determined by means of the thermal analysis and the visual thermal analysis methods. The temperature of a sample (20–50 g) placed in a platinum crucible was registered at a cooling rate of  $4^\circ\text{C min}^{-1}$ . The temperature was measured with a Pt–Pt10Rh thermocouple with a precision of  $\pm 2^\circ\text{C}$ . Because of the glassforming ability of the melts with a higher feldspar content the seeding with small crystals of NaF and the direct observation of the melt (the visual thermal analysis) was used in such cases. The precision of the determination of the temperature of the primary crystallization was then lowered to  $\pm 5^\circ\text{C}$ . Samples containing 0–19 mole % of  $\text{NaAlSi}_3\text{O}_8$  and 0–26 mole % of  $\text{KAlSi}_3\text{O}_8$ , respectively, were examined.

### Results and discussion

The experimentally determined temperatures of primary crystallization of NaF of the examined samples of the NaF– $\text{NaAlSi}_3\text{O}_8$  system are shown as open circles in Fig. 1. The system NaF– $\text{NaAlSi}_3\text{O}_8$  is an internal section of the concentration tetrahedron of the quaternary system NaF– $\text{Na}_2\text{O}$ – $\text{Al}_2\text{O}_3$ – $\text{SiO}_2$ .

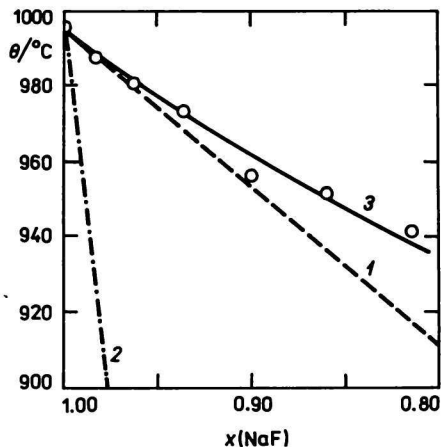


Fig. 1. The liquidus curve of NaF in the NaF– $\text{NaAlSi}_3\text{O}_8$  system. 1. Ideal behaviour; 2. total dissociation of  $\text{AlSi}_3\text{O}_8^-$ ; 3. regular behaviour with  $\Delta E = 21 \text{ kJ mol}^{-1}$ ;  $\circ$  experimental.

Because of the possibility of the substitution of oxygen by fluorine, the investigated system is also a subsystem of the reciprocal system  $\text{Na}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Si}^{4+} \parallel \text{F}^-$ ,  $\text{O}^{2-}$ . Therefore, certain reactions may be expected to take place in the pseudobinary  $\text{NaF}$ — $\text{NaAlSi}_3\text{O}_8$  system.

Three different situations were considered in the thermodynamic analysis of the  $\text{NaF}$ — $\text{NaAlSi}_3\text{O}_8$  system:

i) The system behaves ideally, which means that  $a(\text{NaF}) = x(\text{NaF})$ . For such behaviour the liquidus curve of  $\text{NaF}$  is given by line 1 in Fig. 1 ( $\Delta_f H(\text{NaF}) = 33.57 \text{ kJ mol}^{-1}$  [5]).

ii) The feldspar anions are fully dissociated into  $\text{Al}^{3+}$ ,  $\text{Si}^{4+}$ , and  $\text{O}^{2-}$  in the dilute solutions of feldspar in  $\text{NaF}$  due to the chemical reaction between the fluoride and feldspar anions under formation of other foreign complex ions. In such a case the application of the thermodynamic approach to the activity calculation of components in the network forming silicate systems proposed by Pánek and Daněk [6, 7] yields the following equation for the  $\text{NaF}$  activity

$$a(\text{NaF}) = \frac{4x}{(13 - 11x)^2} \quad (1)$$

where  $x$  is the mole fraction of  $\text{NaF}$  in the initial mixture. Differentiating eqn (1) with respect to  $x$ , for  $x \rightarrow 1$  we get

$$\lim_{x \rightarrow 1} \frac{a(\text{NaF})}{x(\text{NaF})} = \lim_{x \rightarrow 1} \frac{52 + 44x}{(13 - 11x)^3} = 12 \quad (2)$$

which means that in such a case twelve new particles,  $\text{Al}^{3+}$ ,  $3 \text{ Si}^{4+}$ , and  $8 \text{ O}^{2-}$ , are introduced into the  $\text{NaF}$  melt by addition of one molecule of sodium feldspar. Such behaviour of the  $\text{NaF}$ — $\text{NaAlSi}_3\text{O}_8$  system is depicted by line 2 in Fig. 1.

iii) No chemical reaction takes place in the liquid state between the  $\text{NaF}$  and sodium feldspar. However, the components do not mix ideally and at replacement of the fluoride anion by a feldspar anion (e.g.  $\text{AlSi}_3\text{O}_8^-$ ) in the first coordination sphere of the sodium atoms a certain interaction energy  $\Delta E$  is required. Such behaviour may be well described by means of the regular solution theory. For the activity of  $\text{NaF}$  the equation

$$a(\text{NaF}) = x \exp \left[ \frac{\Delta E}{RT} (1 - x)^2 \right] \quad (3)$$

may be derived. The course of the liquidus curve of  $\text{NaF}$  using the interaction energy  $\Delta E = 21 \text{ kJ mol}^{-1}$  is represented by line 3 in Fig. 1. It is evident that such behaviour is the most probable one in the  $\text{NaF}$ — $\text{NaAlSi}_3\text{O}_8$  melts. However, there is a relatively high content of calcium oxide in the sodium feldspar used

(see above) which may cause a reciprocal exchange reaction between the calcium oxide and the sodium fluoride. The value of  $18.8 \text{ kJ mol}^{-1}$  at the temperature of  $1200 \text{ K}$  for the standard Gibbs energy of such exchange reaction may be found in the literature [8].

The NaF—KAlSi<sub>3</sub>O<sub>8</sub> system is also an internal section of the quaternary NaF—K<sub>2</sub>O—Al<sub>2</sub>O<sub>3</sub>—SiO<sub>2</sub> system and a subsystem of the reciprocal system  $\text{Na}^+, \text{K}^+, \text{Al}^{3+}, \text{Si}^{4+} \parallel \text{F}^-, \text{O}^{2-}$ . In the reciprocal NaF—KAlSi<sub>3</sub>O<sub>8</sub> subsystem the exchange reaction



takes place, which must be taken into account in the calculation of the activity of NaF in the melt and the equilibrium mole fractions of all four components must be determined. According to eqn (A),  $y$  moles KF and  $y$  moles NaAlSi<sub>3</sub>O<sub>8</sub> are formed in an original mixture of  $x$  moles NaF and  $(1 - x)$  moles KAlSi<sub>3</sub>O<sub>8</sub>. The equilibrium mole fractions  $x^*$  of components are then as follows:  $x^*(\text{NaF}) = x - y$ ,  $x^*(\text{KAlSi}_3\text{O}_8) = 1 - x - y$ ,  $x^*(\text{KF}) = x^*(\text{NaAlSi}_3\text{O}_8) = y$ . The standard Gibbs energy  $\Delta_r G^\circ$  of the exchange reaction with the equilibrium constant  $K_r$  is then given by the following relation

$$\Delta_r G^\circ = -RT \ln K_r = -RT \ln \frac{y^2}{(x - y)(1 - x - y)} \quad (4)$$

Again there are three possible behavioural patterns:

i) The ideal behaviour considering the exchange reaction, *i.e.*  $a(\text{NaF}) = x - y$ . The liquidus curve of NaF for this case using the value of  $\Delta_r G^\circ = 26.5 \text{ kJ mol}^{-1}$  (see below) is represented by line 1 in Fig. 2.

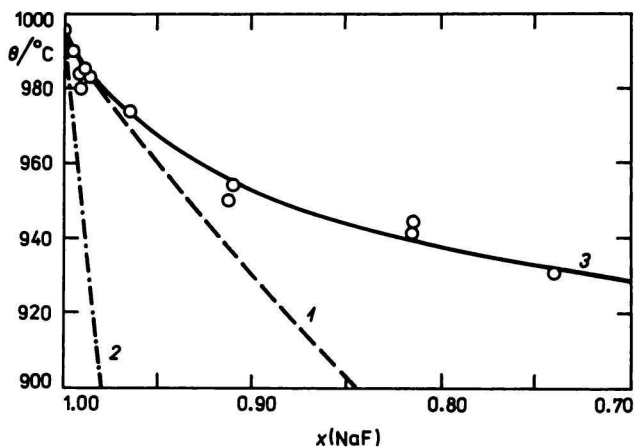


Fig. 2. The liquidus curve of NaF in the NaF—KAlSi<sub>3</sub>O<sub>8</sub> system. 1. Ideal behaviour; 2. total dissociation of AlSi<sub>3</sub>O<sub>8</sub><sup>-</sup>; 3. regular behaviour with regard to the exchange reaction; O experimental.

ii) The total dissociation of the feldspar anion in the dilute solution of potassium feldspar in NaF yields thirteen new particles. Using the thermodynamic approach proposed by *Pánek* and *Daněk* [6, 7] the following expression may be obtained for the activity of NaF

$$a(\text{NaF}) = \left( \frac{2x}{13 - 11x} \right)^2 \quad (5)$$

The liquidus curve for this case is represented by line 2 in Fig. 2.

iii) Assuming the nonideal behaviour, then for the activity of NaF the application of the regular solution theory yields the equation

$$a(\text{NaF}) = x^*(\text{NaF}) \exp \left\{ \frac{\Delta_r G^\circ}{RT} [1 - x^*(\text{NaF})]^2 \right\} \quad (6)$$

The best fit of the experimental and calculated values of the temperature of the primary crystallization was obtained using the value of  $26.5 \text{ kJ mol}^{-1}$  for the standard Gibbs energy of the exchange reaction (*cf.* line 3 in Fig. 2). This value is consistent with the standard Gibbs energy of the exchange reaction  $27.67 \text{ kJ mol}^{-1}$  calculated at the temperature of 1250 K on the basis of the published data of the standard Gibbs energy of the respective components [8] (the high temperature modifications of albite and adularia were considered). Apparently, such behaviour is most probable in the NaF—KAlSi<sub>3</sub>O<sub>8</sub> melts.

## Conclusion

On the basis of the thermodynamic analysis it may be concluded that in the NaF-rich melts of the studied systems probably no chemical reactions between the fluoride and the feldspar anions take place. The systems behave as simple regular solutions. However, the replacement of the fluoride anion by the feldspar one in the first coordination sphere of the alkali cations is accompanied by an interaction energy which is close to the standard Gibbs energy of the exchange reaction between the sodium fluoride and the calcium and potassium oxide, respectively. It may be assumed that the use of the natural feldspars with a certain content of accompanying oxides did not substantially affect the conclusions resulting from the thermodynamic analysis.

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