Measurement of viscosity of fused salts. II.
Viscosity of molten binary mixtures on the cryolite basis

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The viscosity of molten binary $Na_3AlF_6-Al_2O_3$, Na_3AlF_6-LiF, $Na_3AlF_6-Li_3AlF_6$, $Na_3AlF_6-MgF_2$, $Na_3AlF_6-CaF_2$, and Na_3AlF_6-NaCl was measured using the torsion pendulum method. With regard to the electrolytic Al production, the above systems were investigated in the range of high concentrations of cryolite. The measurement was carried out in the temperature interval 850 to 1050°C. The experimental results were interpreted with respect to recent ideas on the structure of melts on the cryolite basis.

In part I of this work [1] some problems dealing with the experimental determination of the viscosity of molten salts, mainly of fluorides and their mixtures, were analyzed and the experimentally determined values of the viscosity of sodium and lithium cryolite were presented. The viscosity of the molten binary mixtures $Na_3AlF_6-Al_2O_3$, Na_3AlF_6-LiF, $Na_3AlF_6-Li_3AlF_6$, $Na_3AlF_6-MgF_2$, $Na_3AlF_6-CaF_2$, and Na_3AlF_6-NaCl was determined. The determination of viscosity of the above systems is interesting from the aspect of the fundamental research, where it can furnish interesting information on the structure of melts on the cryolite basis as well as in regard to the technical practice. Here the influence of different additives on the viscosity of cryolite which is the basic component of the Al electrolyte, is evaluated and compared. From this point of view, mainly the region of high cryolite concentrations is of special interest.

The understanding of the viscosity of the electrolyte is indispensable in the study of hydrodynamic processes in the Al production cell, which play an important role in the electrolytic process, mainly with regard to the circulation and mixing of the electrolyte affected by the electromagnetic fields and thermal gradients, as well as to the transport of anode gases. Furthermore, these processes are closely related to the dissolution of alumina in the electrolyte, to equalizing the temperature differences in the cell as well as to the continuous dissolution of deposited aluminium and the transport of the dissolved metal to the proximity of the anode where it can react with the anode gases. There is also a close relation between the viscosity and the electrical conductivity of the electrolyte. Generally, the electrical conductivity decreases with increasing viscosity and *vice versa*. In addition to this, in the technical process the viscosity can affect the electrical conductivity also indirectly: an increased viscosity impedes the separation of the carbon particles which are suspended in the electrolyte, thus effecting a secondary decrease in the electrical conductivity of the electrolyte.

Regarding the pretentious determination of the viscosity of molten fluorides, the small number of works dealing with these problems is not surprising. From among the binary systems on the cryolite basis, so far only the viscosity of the $Na_3AlF_6-Al_2O_3$ [2, 3], $Na_3AlF_6-CaF_2$ [2, 4], Na_3AlF_6-NaCl [5], $Na_3AlF_6-BaCl_2$ [6], and Na_3AlF_6-

—Li_3AlF_6 [7] mixtures was measured. Considering the substantial differences between the viscosity data about the systems Na_3AlF_6—Al_2O_3 and Na_3AlF_6—CaF_2 and the inadequacy of the published results, the viscosity data in these systems were reexamined and in the system Na_3AlF_6—Li_3AlF_6 the viscosity values in the range of the high cryolite concentration were refined. The viscosity of the molten binary Na_3AlF_6—LiF and Na_3AlF_6—MgF_2 mixtures has not been published as yet.

Experimental

Reagencies

The following reagencies were used for the preparation of samples: Na_3AlF_6 — hand-picked Greenland natural cryolite (m.p. 1006 $\pm$ 1°C, fluorine content determined by the pyrohydrolytic method [8] 54.6% F), Al_2O_3, anal. grade (Reanal, Hungary), Li_3AlF_6 — synthetic, prepared from LiF for single crystals (VÚM, Turnov), AlF_3, prepared by sublimation in a Pt apparatus [9] (99.5% AlF_3), NaCl, anal. grade (Soyuzkhimeksport, USSR), MgF_2 and CaF_2 for single crystals (VÚM, Turnov). Before melting, Na_3AlF_6 and LiF were calcined at 600°C for 3 hours, the remaining reagencies at 300°C for 1—2 hours.

Apparatus

In the measurement of the viscosity, the torsion pendulum method was used. The characteristics of the apparatus were as follows:

Length of the Mo torsion file	540	mm
Diameter of the torsion file	0.15	mm
Mass of the pendulum system	240.6	g
Radius of the Pt sphere at 1000°C	10.24	mm
Period of the amplitude at 1000°C	9.143	
Logarithmic decrement in an inert atmosphere (Ar, N_2) at 1000°C	0.0036	
Calculated decrement in the air át 1000°C	0.0001^5	
Momentum of inertia at 1000°C	296.72	g cm²

The detailed description of the apparatus and of the proceeding in the calculation of viscosity is in part I of this work [1].

In the measurement of the logarithmic decrement of the damped oscillation of the pendulum in the investigated binary mixtures, the refining graphical method [10] was used. For the calculation of the viscosity of the molten binary Na_3AlF_6—Al_2O_3, Na_3AlF_6—LiF, Na_3AlF_6—Li_3AlF_6, and Na_3AlF_6—NaCl, the density values of the respective mixtures as published in [2, 5, 11, 12] were used, whereas in the system Na_3AlF_6—MgF_2 the values presented in [5] and in the system Na_3AlF_6—CaF_2 the values proposed by *Abramov et al.* [2] were accepted.

The temperature was measured using a Pt/Pt10Rh thermocouple with an accuracy of $\pm$1°C. During a single measurement the temperature varied within $\pm$2°C.

Results and discussion

The isotherms of viscosity of the quasi-binary Na_3AlF_6—Al_2O_3 mixtures are presented in Fig. 1. Here, the determined values of viscosity are in good agreement with the data presented by *Abramov et al.* [2]. From the course of the isotherms it follows
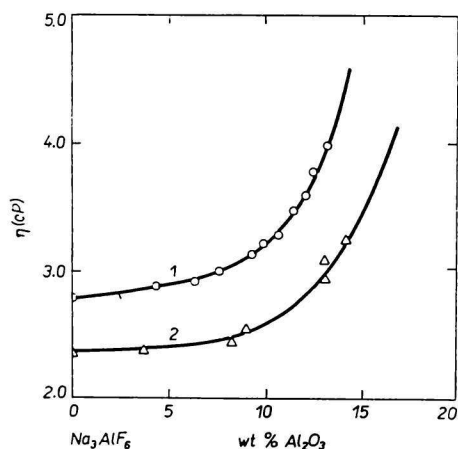
Fig. 1. The isotherms of viscosity of molten $Na_3AlF_6-Al_2O_3$ mixtures. 1. 1000°C; 2. 1050°C.
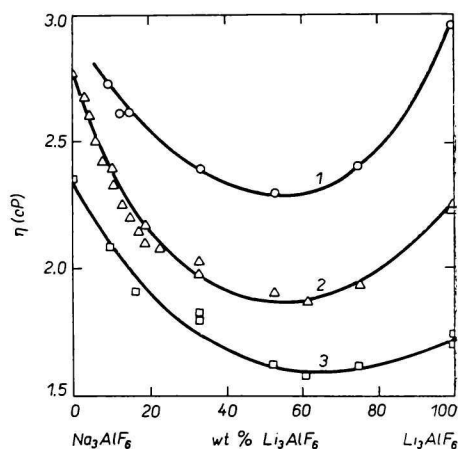

Fig. 2. The isotherms of viscosity of molten $Na_3AlF_6-Li_3AlF_6$ mixtures. 1. 950°C; 2. 1000°C; 3. 1050°C.

that within the range 0—9.8 mole % (0—5 wt %) Al_2O_3 the viscosity remains practically constant. With increasing concentration of alumina, the viscosity rapidly increases and at 29.7 mole % (17 wt %) it attains approx. the double of 2.78 cP, which corresponds to the viscosity of pure cryolite at 1000°C. This value was determined by the extrapolation of the polytherm of the viscosity of cryolite since the m.p. of cryolite is 1006 ± 1°C.
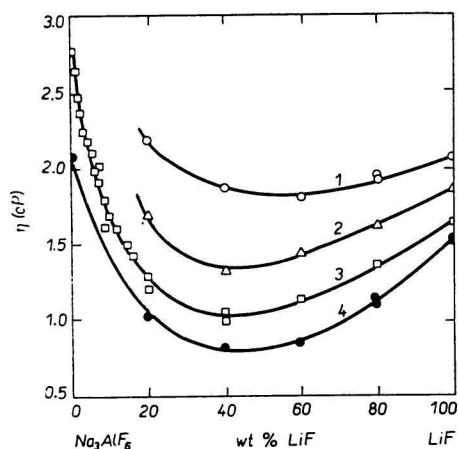

Fig. 3. The isotherms of viscosity of molten Na_3AlF_6-LiF mixtures. 1. 900°C; 2. 950°C; 3. 1000°C; 4. 1050°C.
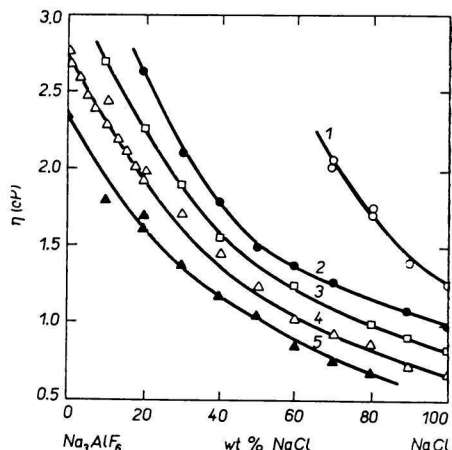

Fig. 4. The isotherms of viscosity of molten Na_3AlF_6-NaCl mixtures. 1. 850°C; 2. 900°C; 3. 950°C; 4. 1000°C; 5. 1050°C.

The determined dependence $\eta_{mix} = f(c_{Al_2O_3})$ can be satisfactorily interpreted on. the basis of the actual information on the structure of the molten $Na_3AlF_6 - Al_2O_3$ mixtures. Generally, it is assumed that the dissolution of alumina in molten cryolite is combined with a complicated interaction of the components which results in the formation of various fluoride oxide complex anions. From the cryoscopic measurements carried out by *Brynestad et al.* [13] it follows that at low Al_2O_3 concentrations, most probably the complex anions $AlOF_2^-$ and $AlOF_3^{2-}$ arise. The presence of these anions does not affect substantially the viscosity of the melt. However, at higher alumina. concentrations, complex anions containing two or three atoms of oxygen are formed. It may be assumed that the formation of these complexes brings about certain increase in the viscosity. The subsequent rapid increase of the viscosity can be explained in the following way: according to *Brynestad et al.* [14], the equilibrium concentration of Al_2O_3 in a saturated solution with cryolite at 1000°C is 25.10 mole % (14 wt %). In the present work, the system $Na_3AlF_6 - Al_2O_3$ was investigated in the concentration. range $0 - 29.7$ mole % (17.0 wt %) Al_2O_3; hence, above the equilibrium concentration either oversaturated solution is formed, or excessive alumina forms a fine suspension, which is accompanied by a marked increase in the viscosity of the melt. A similar case, *i.e.* a large increase in the viscosity of molten NaCl and KCl caused by the suspension of γ-Al_2O_3, was reported by *Belyaev* and *Zhemchuzhina* [15].

The viscosity isotherms of the molten $Na_3AlF_6 - Li_3AlF_6$ mixtures (Fig. 2) pass through a minimum. The experimentally determined values of viscosity are little higher than those reported by *Vetyukov* and *Sipriya* [7]; however, in both cases the course of the isotherms is identical. According to *Kurnakov* and *Zhemchuzhnyi* [16], a minimum on the isotherms of viscosity indicates the dissociation of complex or associated constituents. In the investigated system, evidently the complex anion AlF_6^{3-} dissociates with the formation of AlF_4^- and F^- ions. The increasing dissociation of the AlF_6^{3-} anion cannot be caused by the gradual exchange of the cations Na^+ for Li^+ with increasing concentration of Li_3AlF_6 in the melt, since, in such a case the minimum should coincide with
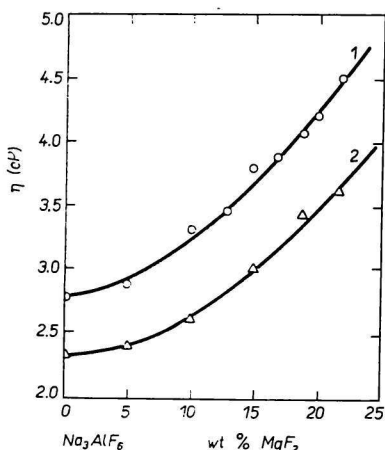

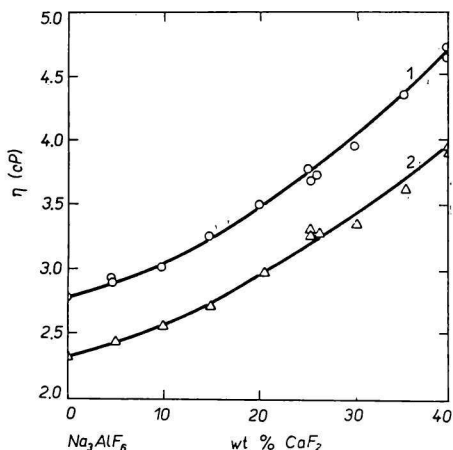*Fig. 5.* The isotherms of viscosity of molten $Na_3AlF_6 - MgF_2$ mixtures. *1.* 1000°C; *2.* 1050°C.

Fig. 6. The isotherms of viscosity of molten $Na_3AlF_6 - CaF_2$ mixtures. *1.* 1000°C; *2.* 1050°C.

pure Li_3AlF_6 (and *vice versa*, with pure Na_3AlF_6). Hence, it may be assumed that the dissociation of the complex anion is affected mainly by the relative overheating of the melt with respect to the liquidus temperature in the system $Na_3AlF_6 - Li_3AlF_6$.

The course of the isotherms of viscosity of the molten $Na_3AlF_6 - LiF$ mixtures (Fig. 3) is similar as in the above system. In this case, the existence of the minimum seems to be surprising since the introduction of F^- ions into the melt should suppress the
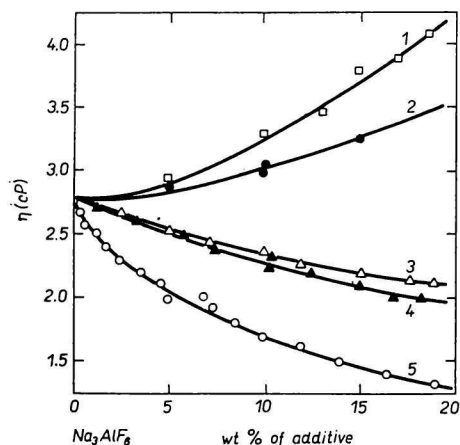

Fig. 7. The influence of different additives on the viscosity of cryolite at 1000°C.
1. MgF_2; 2. CaF_2; 3. Li_3AlF_6; 4. NaCl; 5. LiF.

dissociation of the complex AlF_6^{3-} anions. Besides, in molten LiF there are no voluminous complex ions which could bring about an increase in the viscosity of the melt in the range of high concentrations of LiF. It ensues from this that also in this case the effect of the relative overheating ought to be considered.

The viscosity of the molten $Na_3AlF_6 - NaCl$ monotonously decreases with increasing concentration of NaCl within the whole concentration range (Fig. 4). This course results most probably from the gradually changing structure of the melt, *i.e.* the decreasing concentration of the complex anions AlF_6^{3-} and AlF_4^-, and the increasing concentration of the mobile Na^+ and Cl^- ions, as well as from the relatively increasing overheating of the melt with respect to the liquidus temperature [17].

In the systems $Na_3AlF_6 - MgF_2$ and $Na_3AlF_6 - CaF_2$, the viscosity was measured in the concentration range where the temperature of the primary crystallization of the respective mixtures did not exceed 1050°C (Figs. 5 and 6). The determined values of viscosity of the $Na_3AlF_6 - CaF_2$ mixtures are in good agreement with the corresponding values reported by *Abramov et al.* [2]. In both systems, the viscosity increases with increasing concentration of the alkaline earth fluoride. This increase in the viscosity is more pronounced in the case of MgF_2, most probably owing to the complex-forming activity of the Mg^{2+} cations. According to *Vakhobov* and *Belyaev* [18], MgF_2 dissolves in molten cryolite with the formation of the complex MgF_3^- anions, this causing an increase in the viscosity of the melt. Allegedly, the increasing viscosity is responsible for the decrease of the electrical conductivity which is effected by the additions of alkaline earth fluorides. Here also, the negative influence of MgF_2 is more marked than that of CaF_2. However, from an analysis of the experimental data it follows that the increase in the viscosity cannot be attributed only to the complex-forming activity since in

the case of an addition of CaF_2^- no calcium-containing complex ions were determined in the melt. It may be assumed that in this case, the increase of the viscosity is effected by the introduction of F^- anions into the melt which suppress the dissociation of the AlF_6^{3-} complex anions.

For ease of comparison of the influence of the individual additives on the viscosity of cryolite, in Fig. 7 the isotherms of the viscosity at 1000°C of the respective systems in the concentration range $0-20$ wt % addition, which is most interesting from the technical aspect, are presented. The analysis of the determined dependences of viscosity and the comparison with the electrical conductivity data of the investigated systems [19—21], confirmed the relation between the viscosity and the specific electrical conductivity of the corresponding molten binary mixtures.

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