Viscosity of Sodium Cryolite + Aluminum Fluoride + Potassium Fluoride Melts

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The viscosity of the molten system Na_3AlF_6 + AlF_3 + KF + (Al_2O_3) was investigated using a torsional oscillating cylinder viscometer. The melts contained up to 25 mass % AlF_3 and 5.85 mass % KF. The temperature ranged from 865 to 1030 °C. The method was absolute, and the accuracy of the viscosity data of cryolite-based melts was better than 3%. The product ηV where η is the viscosity and V the molar volume can be described by the equation $\eta V/(\text{mPa·s·cm}^3\text{·mol}^{-1}) = 800.13 - 0.585t/°C - 3.314w(AlF_3) + 25.027w(KF) - 35.614w(Al_2O_3) - 1.726w(AlF_3)w(KF) + 2.577w(AlF_3)w(Al_2O_3)$ where $w(AlF_3)$ denotes the mass percent of excess aluminum fluoride with respect to cryolite.

Introduction

The molten systems based on cryolite (Na_3AlF_6) serve as the solvent for alumina in the electrolytes used for production of aluminum (Grjotheim et al., 1982). The high melting temperature of cryolite (1011 °C) can be lowered by the additions of other salts. The conventional system consists of cryolite with 6–13% AlF_3, 3–8% CaF_2, and 2–5% Al_2O_3 (all percentages by mass). The working temperature of the electrolyte is usually in the range 945–970 °C. It might be of advantage to use an electrolyte with a lower melting temperature (Fellner et al., 1993; Grjotheim et al., 1982; Thonstad and Solheim, 1986). The temperature of primary crystallization can be lowered by use of the AlF_3-rich bath and/or by the introduction of certain additives. Besides the additions like CaF_2, LiF, and MgF_2, potassium fluoride may also be present in the bath. The effect of the addition of KF on the temperature of primary crystallization of the system Na_3AlF_6 + AlF_3 has been studied by Gabčová et al. (1995). The electrical conductivity of this system was discussed by Híveš et al. (1994). Knowledge of the viscosity of the mixture is important to understand and optimize the hydrodynamic processes in the electrolyzer used for production of aluminum. Recently we reported the viscosity of the system Na_3AlF_6 + AlF_3 + LiF (Fellner and Silný, 1994). In this work we have measured the effect of KF on the viscosity of the molten system Na_3AlF_6 + AlF_3.

Experimental Section

Sodium fluoride of grade "for monocrystals" was used. Potassium fluoride was of grade "pro analysis" and it was first dried in a vacuum furnace at room temperature in the presence of P_2O_5 for 10 days and then at 130 °C for 48 h. Aluminum fluoride (technical) was purified by sublimation in a platinum apparatus under atmospheric pressure. The final product was typically of purity 99.6%; the rest was alumina. Alumina was of grade pro analysis. The Na_3AlF_6 + AlF_3 + KF + (Al_2O_3) mixtures were prepared by mixing NaF with the appropriate known masses of AlF_3, KF, and Al_2O_3. The sample preparation was made in a glovebox and then quickly transferred into the furnace where it was under an atmosphere of dried argon.

The torsional oscillating cylinder viscometer was used for the viscosity measurements. The viscometer measures the damping of the cylinder oscillating in contact with the melt. Absolute viscosity was calculated from the logarithmic decrement. The length of torsional wire (Pt8%W, diameter 0.3 mm) is 540 mm, and the cylinder is made of platinum. The digital data acquisition system is computer facilitated and highly automated. The experimental procedure of the viscosity measurement has been described in detail in our previous paper (Fellner and Silný, 1994).

The standard deviation of the viscosity of molten potassium chloride was found to be 1.5×10^{-3} mPa·s. The standard deviation of the viscosity of the system Na_3AlF_6 + AlF_3 + KF + Al_2O_3 calculated for a given composition was found to be lower than 2×10^{-2} mPa·s. The standard deviation in temperature determination did not exceed 0.3 °C. The main source of error is the uncertainty in the composition of the melt caused by evaporation and by impurities of alumina in aluminum fluoride used for preparation of the melt. It can be estimated that the uncertainty in the viscosity is about 3%.

Results and Discussion

Six Na_3AlF_6 + AlF_3 + KF + (Al_2O_3) mixtures were investigated (some of them repeatedly) in the temperature range 865–1030 °C. The results are summarized in Table 1. It was found that the experimental results could be described by the following equation:

$$\eta V/(\text{mPa·s·cm}^3\text{·mol}^{-1}) = 800.13 - 0.585t/°C - 3.314w(AlF_3) + 25.027w(KF) - 35.614w(Al_2O_3) - 1.726w(AlF_3)w(KF) + 2.577w(AlF_3)w(Al_2O_3) \quad (1)$$

where η is the viscosity and V the molar volume of the mixture. The coefficients of the equation were determined using a multiple-linear regression. The composition is given in mass percent. $w(AlF_3)$ denotes the mass percent of excess aluminum fluoride with respect to cryolite. The standard deviation was found to be 1.93 mPa·s·cm^3·mol^{-1}, which is about 1.5%.

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Table 1. Experimental Data on the Viscosity, η, of the Molten System $Na_3AlF_6 + AlF_3 + KF + Al_2O_3$[a]

$w(AlF_3)$	$w(KF)$	$w(Al_2O_3)$	t/°C	η/(mPa·s)	Δ	$w(AlF_3)$	$w(KF)$	$w(Al_2O_3)$	t/°C	η/(mPa·s)	Δ
10.0	2.50	0.0	994.5	2.274	−0.036	20.0	5.00	0.0	915.9	1.805	−1.509
10.0	2.50	0.0	992.4	2.317	1.156	20.0	5.00	0.0	906.3	1.874	−1.830
10.0	2.50	0.0	984.3	2.406	2.322	20.0	5.00	0.0	896.9	1.968	−0.781
10.0	2.50	0.0	982.5	2.426	2.595	20.0	5.00	0.0	887.1	2.038	−1.191
10.0	2.50	0.0	1002.0	2.237	0.822	20.0	5.00	0.0	876.7	2.160	0.594
10.0	2.50	0.0	1012.1	2.155	0.514	20.0	5.00	0.0	865.1	2.227	−0.729
10.0	2.50	0.0	1022.2	2.075	0.228	20.0	5.00	0.0	871.3	2.132	−2.738
10.0	2.50	0.0	1031.9	2.006	0.291	20.0	5.00	0.0	880.8	2.059	−2.618
10.0	2.50	0.0	1024.3	2.047	−0.409	20.0	5.00	0.0	890.2	1.995	−2.102
10.0	2.50	0.0	1015.0	2.117	−0.295	20.0	5.00	0.0	900.7	1.935	−0.913
10.0	2.50	0.0	1005.1	2.195	−0.046	20.0	5.00	0.0	910.9	1.877	0.256
10.0	2.50	0.0	995.5	2.281	0.604	20.0	5.00	0.0	921.2	1.823	1.824
10.0	2.50	0.0	985.3	2.367	1.012	10.0	5.00	3.0	998.0	2.104	−0.951
10.0	2.50	0.0	975.5	2.462	1.837	10.0	5.00	3.0	991.7	2.108	−2.870
10.0	2.50	0.0	965.7	2.560	2.737	10.0	5.00	3.0	983.4	2.193	−1.761
10.0	2.50	0.0	1013.5	2.096	−1.798	10.0	5.00	3.0	973.8	2.288	−0.697
10.0	2.50	0.0	1005.7	2.157	−1.599	10.0	5.00	3.0	963.9	2.384	0.233
10.0	2.50	0.0	996.4	2.238	−0.997	10.0	5.00	3.0	954.0	2.495	1.664
10.0	2.50	0.0	986.8	2.323	−0.393	10.0	5.00	3.0	944.0	2.598	2.673
10.0	2.50	0.0	976.9	2.416	0.366	10.0	5.00	3.0	953.0	2.456	−0.204
10.0	2.50	0.0	984.1	2.345	−0.321	20.0	5.00	3.0	958.8	2.091	−0.382
10.0	2.50	0.0	993.6	2.263	−0.830	20.0	5.00	3.0	951.7	2.179	1.092
10.0	2.50	0.0	1003.6	2.177	−1.359	20.0	5.00	3.0	942.6	2.290	2.740
10.0	2.50	0.0	1013.4	2.099	−1.665	20.0	5.00	3.0	923.6	2.413	1.204
10.0	2.50	0.0	1023.6	2.023	−1.818	20.0	5.00	3.0	913.6	2.417	−2.039
10.0	2.50	0.0	1033.2	1.954	−1.837	20.0	5.00	3.0	904.0	2.511	−1.422
18.1	5.85	0.0	979.3	1.549	1.835	20.0	5.00	3.0	909.2	2.460	−1.745
18.1	5.85	0.0	969.5	1.605	0.669	20.0	5.00	3.0	918.0	2.367	−2.627
18.1	5.85	0.0	960.2	1.645	−1.173	20.0	5.00	3.0	928.5	2.287	−2.428
18.1	5.85	0.0	950.5	1.695	−2.480	20.0	5.00	3.0	939.1	2.211	−2.080
20.0	2.50	0.0	954.5	1.905	2.859	20.0	5.00	3.0	949.3	2.128	−2.185
20.0	2.50	0.0	944.7	1.981	2.616	20.0	5.00	3.0	959.5	2.060	−1.585
20.0	2.50	0.0	935.1	2.062	2.738	20.0	5.00	3.0	969.8	1.995	−0.819
20.0	5.00	0.0	935.5	1.695	1.008	20.0	5.00	3.0	980.2	1.937	0.383
20.0	5.00	0.0	925.8	1.735	−1.118						

[a] The deviation from calculated values, Δ, is given by eq 3.

The molar volume was calculated according to the equation

$$V/(\mathrm{cm^3 \cdot mol^{-1}}) = [1 + 4.3754 \times 10^{-4}(t/°\mathrm{C} - 900)][95.693x(Na_3AlF_6) + 73.0x(Li_3AlF_6) + 74.303x(NaAlF_4) - 20.0x(Na_3AlF_6)x(NaAlF_4) + 130.8x(K_3AlF_6) + 57.5x(Al_2O_3)] \quad (2)$$

In eq 2 $x(i)$ denotes the mole fractions of the components obtained according the following model: (i) No free AlF_3 or KF is present in the melt. (ii) All KF reacts with excess AlF_3 and forms K_3AlF_6. (iii) All AlF_3 remaining after step ii reacts with Na_3AlF_6 and forms $NaAlF_4$ according to the reaction scheme $Na_3AlF_6 + 2AlF_3 \rightleftharpoons 3NaAlF_4$. These assumptions do not reflect precisely the real structure of the melt, but the model is closer to reality than the assumption of the existence of free AlF_3 and/or KF in the melt.

This equation is based on our experimental data, and it differs from that used in Fellner and Silný (1994) by introduction of the term expressing the influence of the KF addition on the molar volume of cryolite-based melts. The parameter describing the molar volume of K_3AlF_6 was estimated using data published by Perez (1986) and also by Chrenková and Fellner (1991). The experimental and calculated data are compared in Table 1 and Figure 1.

The coefficient of regression, r^2, has a value of 0.994. The difference between the experimental and calculated viscosity values is given by

$$\Delta = 100[\eta(\mathrm{exptl}) - \eta(\mathrm{calcd})]/\eta(\mathrm{exptl}) \quad (3)$$

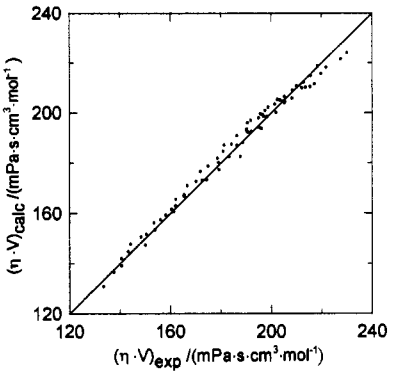

Figure 1. Comparison between experimental and calculated values of the viscosity.

The viscosity equation proposed in this work describes the viscosity of a molten mixture of $Na_3AlF_6 + AlF_3 + KF + Al_2O_3$ well in the temperature and concentration range studied. The major source of error in the viscosity values is the uncertainty in the composition of the melt. This results from the evaporation of the melt (vapors consists mainly of $NaAlF_4$) and impurity of alumina (less then 0.5 mass %) in sublimed aluminum fluoride. With respect to these uncertainties the accuracy of the viscosity values was estimated to be 3%. The equation of the viscosity agrees with the experimental values within this uncertainty.

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