Electrical Conductivity and Density of Cryolite-Base Melts

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1 INTRODUCTION

Cryolite-base, $\text{Na}_3\text{AlF}_6\text{-AlF}_3\text{-CaF}_2$ melts are well-known solvents for alumina and have been the major components of electrolytes for the production of aluminium. The electrical conductivity and density of a cryolite-base melt have long been both of theoretical interest and practical significance. Although a number of measured values of these properties for binary and ternary melts are available¹⁻⁴), data vary considerably and reliable ones are scarce, mainly because of the corrosive nature of the pertinent melts and the frequency dispersion of the measured conductivity. For industrially important quaternary melts, previous conductivity measurements are moreover scarce^{3,5-7}).

In the laboratory measurements of resistivity (the inverse of conductivity) of the quaternary melts, Gaspard et al.⁵) once reported that the resistivity of a bath containing 6 mass% (designated as % hereafter) CaF_2 showed an abnormal decrease at ca. 6% Al_2O_3 and the decrease became maximum with the bath containing 6% AlF_3 . They inferred a change of the melt structure with the anomaly. They could not observe, however, the anomaly in the industrial pots.

Our objects are to obtain frequency-independent, reliable conductivity data for industrial standard baths and to reinvestigate the above-mentioned anomaly with the help of measurements of density which also has a strong relationship with the melt structure.

2 EXPERIMENTAL

Reagent-grade chemicals were used. Measuring samples were premelted. The compositions of solvent baths were varied as follows: AlF_3 , 3%, 6%, and 9%; CaF_2 , 3%, and 6%; and Na_3AlF_6 , the remainder. The Al_2O_3 contents of measuring samples were varied within 0-8% by 0.5 or 1% increments.

The apparatus employed for conductivity measurements using a platinum conductivity cell similar to the one reported by Bajcsy et al.⁸) is illustrated in our previous abstract⁶). We used, however, a

platinum hemispherical electrode as a container for a melt in place of a separate crucible as described earlier by Fay⁹). A platinized-platinum rod with a hemispherical lower end was immersed as the other electrode into the melt.

The ac bridge used was the Kelvin bridge (Shimadzu, Type BF-902). A sinusoidal wave (1-50 kHz) was applied to the bridge with an oscillator (Hewlett-Packard, Type 204C), and bridge balance was obtained with a tuned null detector (Yokokawa/Hewlett-Packard, Type 4403 A). The conductivity measurements were carried out typically at 1273 K.

Using the platinum black on the rod electrode for each run and balancing the reactance of a measuring melt with a variable capacitance connected to the standard resistance of the bridge first enabled us to virtually eliminate the frequency-dependence of the measured resistance at frequencies over 7 kHz. We regarded the measured resistance for these frequency range as polarization resistance-free, i.e., as purely ohmic, whereas most of the previous reports employed some extrapolation procedures^{1,4}), which is one of the major sources of error, to obtain the resistance at infinite frequency. By the use of the double bridge, we were able to measure a small resistance of the cell, such as less than 0.2 Ω , excluding a much larger lead resistance.

The cell constants were obtained at ambient temperatures at six precise immersion depths of the rod electrode with standard aqueous KCl solutions. Equation (1), first developed by Fay⁹), has been established between these cell constants, K_{cell} , and the measured values of the resistance, R , of the melt at the corresponding immersion depths,

$$R = \rho K_{\text{cell}} + R_{\text{lead}} \quad (1)$$

where, ρ is the resistivity of the melt, and R_{lead} , the lead resistance (substantially zero in our case). From the slope of Eq. (1), we can obtain the resistivity, ρ .

The validity of this treatment has been confirmed with preliminary measurements for some melts including pure cryolite, for which a commonly accepted literature value was reported^{3,4}).

The densities were measured at a series of temperatures by the hydrostatic weighing method using a platinum sinker as described previously¹⁰).

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Fig. 1 Dependence of resistivity of $[\text{Na}_3\text{AlF}_6\text{-}6\%\text{AlF}_3\text{-}6\%\text{CaF}_2]\text{-Al}_2\text{O}_3$ melts on Al_2O_3 content.
 ○: This work. △: Gaspard et al.⁵⁾ (at 1263 K).
 □: Gaspard et al.⁵⁾ (at 1283 K). ---: Vidament and Rey cited in ref. 3 (solv.: 6% $\text{AlF}_3\text{-}5\%\text{CaF}_2$ at liquidus temp.). ---: Fellner et al.'s reg. eq.¹²⁾.

3 RESULTS AND DISCUSSION

Figure 1 shows the dependence of our measured values of the resistivity on the Al_2O_3 content in the bath, in which Gaspard et al.⁵⁾ observed the most abnormal decrease. In Fig. 1 we also show relevant literature data^{3,5)} and calculated values with the regression equation first derived by Choudhary¹¹⁾ and later modified by Fellner et al.¹²⁾ for the conductivity as a function of both composition and temperature from reliable data. All the curves in Fig. 1, except for Gaspard et al.'s, show no abnormal changes around 6% Al_2O_3 . Our resistivity data (not shown) obtained in the 3% $\text{AlF}_3\text{-}6\%\text{CaF}_2$ solvent bath, in which Gaspard et al. also observed a slightly abnormal change, show no anomaly.

Figure 2 shows our resistivity data for two solvent baths both containing 3% CaF_2 . In these melts again we observe no anomalies. Our data in Fig. 2 agree well with those calculated with the regression equation of Fellner et al.

Figure 3 shows the dependence of our density data of related melts on the Al_2O_3 content at 1273 K, together with typical literature data^{1,2)} for the $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3$ melt. All the plots in Fig. 3, and the other plots (not shown) obtained by us at different temperatures, and of literature data for pertinent

Fig. 2 Dependence of resistivity of $[\text{Na}_3\text{AlF}_6\text{-AlF}_3\text{-}3\%\text{CaF}_2]\text{-Al}_2\text{O}_3$ melts on Al_2O_3 content.

○: This work (solv.: 6% $\text{AlF}_3\text{-}3\%\text{CaF}_2$). △: This work (solv.: 9% $\text{AlF}_3\text{-}3\%\text{CaF}_2$). ---: Fellner et al.'s reg. eq.¹²⁾ (solv.: 6% $\text{AlF}_3\text{-}3\%\text{CaF}_2$). ---: Fellner et al.'s reg. eq.¹²⁾ (solv.: 9% $\text{AlF}_3\text{-}3\%\text{CaF}_2$).

Fig. 3 Dependence of density of $\text{Na}_3\text{AlF}_6\text{-AlF}_3\text{-CaF}_2\text{-Al}_2\text{O}_3$ and $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3$ melts on Al_2O_3 content.
 ○: This work (solv.: 6% $\text{AlF}_3\text{-}3\%\text{CaF}_2$). △: This work (solv.: 6% $\text{AlF}_3\text{-}6\%\text{CaF}_2$). □: This work (solv.: 9% $\text{AlF}_3\text{-}3\%\text{CaF}_2$). ●: Edwards et al.¹⁾
 ■: Matiašovský and Malinovský²⁾.

melts demonstrate a nearly linear relationship, around 6% Al_2O_3 , with the Al_2O_3 content, which seems to deny the change, near 6% Al_2O_3 , of the melt structure or the change of the species of the complex ions generally believed to be formed.

In conclusion, the present results resolve the anomaly reported in the previous work⁵⁾ for the baths near the industrial standard compositions and confirm the tendency predicted from the previous regression equations, although melt structure even when Al_2O_3 is added to Na_3AlF_6 is not yet well established. The data obtained by Gaspard et al.⁵⁾ in the industrial pots and those by Wang et al.⁷⁾ in the laboratory also support the conclusion.

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