

Electrical conductivity of molten binary $\text{Na}_3\text{AlF}_6\text{--NaCl}$ and $\text{Na}_3\text{AlF}_6\text{--BaCl}_2$ mixtures

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The specific electrical conductivity of molten binary $\text{Na}_3\text{AlF}_6\text{--NaCl}$ and $\text{Na}_3\text{AlF}_6\text{--BaCl}_2$ mixtures was measured and on the basis of the experimentally determined values the isotherms of the specific conductivity of the above mixtures were plotted. For the hypothetical conductivity of molten cryolite at 1000°C the extrapolated value $2.80\text{ ohm}^{-1}\text{ cm}^{-1}$ was accepted, whereas for pure components NaCl and BaCl_2 the specific conductivity values 4.14 and $2.17\text{ ohm}^{-1}\text{ cm}^{-1}$, respectively, were determined at the same temperature. The experimental results were interpreted with respect to the recent assumptions on the structure of the melts on the cryolite basis.

The main purpose of the study of the specific electrical conductivity of molten binary $\text{Na}_3\text{AlF}_6\text{--NaCl}$ and $\text{Na}_3\text{AlF}_6\text{--BaCl}_2$ mixtures was to determine the influence of admixtures of NaCl and BaCl_2 on the electrical conductivity of the basic Al electrolyte which appears to be of prime importance with regard to the technical process [1, 2].

The electrical conductivity of molten $\text{Na}_3\text{AlF}_6\text{--NaCl}$ mixtures was measured by several authors [3–7]. With regard to the possibility of the industrial application, mainly the region with high cryolite concentration was studied. The data reported by different authors differ in both the presented conductivity values of pure cryolite and the character of the conductivity isotherms at 1000°C .

The electrical conductivity of molten $\text{Na}_3\text{AlF}_6\text{--BaCl}_2$ mixtures was measured by *Belyaev et al.* [6, 8–10]. According to the above cited works, the dependence $\sigma = f(c_{\text{BaCl}_2})$ passes through a maximum. The concentration co-ordinate of this maximum is reported to be between 5 and 10 mole % BaCl_2 . However, this course of conductivity isotherms seems to be highly improbable and it was criticized before [1, 2].

In the present work, the results of determination of the electrical conductivity of the molten binary $\text{Na}_3\text{AlF}_6\text{--NaCl}$ and $\text{Na}_3\text{AlF}_6\text{--BaCl}_2$ in the entire concentration region are presented. The course of the dependence $\sigma = f(c_{\text{NaCl}})$ is interpreted with regard to recent assumptions on the structure of the cryolite melts and the dependence $\sigma = f(c_{\text{BaCl}_2})$ is discussed with respect to the possible interaction of the components.

Experimental

Experimental technique

The conductivity cell consisted of a Pt crucible with two disc electrodes of bright Pt ($d = 5\text{ mm}$), each being procured by a current and a voltage inlet (Pt30Ir wire, $d = 0.5\text{ mm}$). The inter-polar distance was 12 mm . The electrodes were immersed 7 mm

deep in the melt (the upper edge), using a micrometric screw with an accuracy of ± 0.01 mm.

The cell constant was determined by means of molten cryolite, Na_3AlF_6 . For the hypothetical conductivity of cryolite at 1000°C , the value $2.80 \cdot \text{ohm}^{-1} \text{cm}^{-1}$ reported by *Edwards et al.* [11], and later confirmed by *Yim and Feinleib* [12] and by *Bajcsy et al.* [13], was accepted. For the determination of the resistivity of the melt, a transformer bridge of the Wayne—Kerr type was used. It was fed by a tone generator at the frequency 50 kHz. A nanovoltmeter, type Unipan, was used as zero indicator. The measurement was carried out with a current of 10 mA. The average error of an individual measurement was $\pm 2\%$. A detailed description of the applied technique was presented previously [14, 15].

For the measurement of temperature, a Pt/Pt10Rh thermocouple was used, the hot junction being situated between the electrodes. The alternating voltage induced into the thermocouple was eliminated using a frequency filter, designed and constructed for this purpose. The temperature was measured with an accuracy of $\pm 1^\circ\text{C}$.

Reagencies

For the preparation of samples, the following reagencies were used:

Na_3AlF_6 , hand-picked natural Greenland cryolite (m.p. $1006 \pm 1^\circ\text{C}$, the fluorine content determined by pyrohydrolytic method [16] was 54.72% F).

NaCl , anal. grade, Soyuzkhimeksport, USSR.

BaCl_2 , anal. grade, Lachema, dehydrated by vacuum calcination at 200°C for 2 hours.

The total amount of the sample was 15 g.

Results and discussion

On the basis of the experimentally determined values (Tables 1 and 2) the isotherms of the specific electrical conductivity of the studied systems were plotted (Figs. 1 and 2).

The experimentally determined values of the specific conductivity of pure components, NaCl and BaCl_2 at 1000°C , 4.14 and $2.17 \text{ ohm}^{-1} \text{cm}^{-1}$, respectively, are practically identical with the values calculated according to the equations proposed by *Janz et al.* [17].

The determined values of the specific conductivity of molten binary Na_3AlF_6 — NaCl mixtures are substantially higher than those reported by *Vajna* [3] and lower than the data presented by *Kuvakin* and *Kusakin* [4] and by *Vakhobov* and *Belyaev* [6]. The character of the dependence $\sigma = f(c_{\text{NaCl}})$ differs entirely from that mentioned in the cited works, and it is practically identical with the course presented by *Matiašovský et al.* [5, 7]. The determined conductivity values are by 3—5% lower than the corresponding values reported in the above works [5, 7], this being practically within the experimental error. The marked influence of the addition of NaCl on the electrical conductivity in the range of low concentrations of sodium chloride, which was stated by *Vakhobov* and *Belyaev* [6], was not confirmed. The measured specific electrical conductivity values were found to be lower than the corresponding additive values in the entire concentration range. The incorrect conductivity values determined by *Vajna* [3], *Kuvakin* and *Kusakin* [4] and by *Vakhobov* and *Belyaev* [6] are most probably caused by an inadequate measuring scheme or by a low frequency of the measuring current which is extremely important in the measurement of the electrical conductivity of molten salts, especially of fluorides and chlorides [15, 18].

The singular course of the isotherms of the specific conductivity can be interpreted

Table 1

Specific electrical conductivity, σ , of molten binary Na_3AlF_6 — NaCl mixtures

Concentration of NaCl wt %/mole %		—	5.0/15.8	10.0/28.5
Temperature [°C]	σ [ohm ⁻¹ cm ⁻¹]	1100 3.05*	1091 3.07	1065 3.06
		1050 2.94*	1061 3.02	1041 3.02
		1000 2.80*	1033 2.94	1018 2.96
			1006 2.88	993 2.89
			982 2.82	977 2.84
15.0/38.8	20.0/47.4	30.0/60.6	40.0/70.5	50.0/78.2
1084 3.14	1075 3.12	1052 3.09	1051 3.15	1053 3.28
1056 3.08	1052 3.07	1022 3.03	1028 3.12	1024 3.24
1032 3.03	1028 3.02	995 2.96	1006 3.08	999 3.19
1011 2.98	1008 2.97	967 2.90	973 3.01	969 3.15
991 2.92	986 2.92	946 2.87	952 2.96	948 3.10
972 2.87	966 2.85	928 2.80	931 2.92	928 3.06
60.0/84.2	70.0/89.3	80.0/93.5	90.0/97.1	100
1068 3.41	1056 3.61	1037 3.76	1047 4.00	1058 4.25
1044 3.38	1029 3.56	1010 3.74	1022 3.96	1037 4.21
1023 3.35	1003 3.54	983 3.70	1000 3.94	1013 4.16
1003 3.32	975 3.50	961 3.66	973 3.90	989 4.14
975 3.28	951 3.46	942 3.62	950 3.87	962 4.05
959 3.27	932 3.42	923 3.58	928 3.83	933 3.98
942 3.22			910 3.80	

* Values reported by *Edwards et al.* [11].

Table 2

Specific electrical conductivity, σ , of molten binary Na_3AlF_6 — BaCl_2 mixtures

Concentration of BaCl ₂ wt %/mole %		—	2.0/2.0	5.0/5.0
Temperature [°C]	σ [ohm ⁻¹ cm ⁻¹]	1100 3.05*	1110 3.02	1120 2.75
		1050 2.94*	1050 2.85	1100 2.73
		1000 2.80*	1015 2.75	1070 2.70
			1010 2.75	1050 2.68
			1000 2.71	1030 2.67
		990 2.67	1015 2.63	
		985 2.66		
10.0/10.1	20.0/20.1	40.0/40.2	60.0/60.2	100
1070 2.60	1120 2.62	1050 2.41	1060 2.35	1080 2.43
1050 2.57	1060 2.49	1035 2.36	1040 2.31	1060 2.33
1030 2.53	1035 2.45	1025 2.34	1030 2.29	1035 2.28
1010 2.51	1020 2.41	1015 2.30	1010 2.22	1020 2.28
990 2.47	1010 2.37	1010 2.30	995 2.19	990 2.11
980 2.46	995 2.34	1000 2.27	970 2.04	975 2.09
	970 2.25	990 2.22	950 1.98	

* Values reported by *Edwards et al.* [11].

— at least qualitatively — on the basis of recent assumptions on the structure of the cryolite melts. According to *Matiašovský* and *Daněk* [19], in molten cryolite, the anions F^- , AlF_4^- , and AlF_6^{3-} , the cations Na^+ and the associated ionic pairs Na^+F^- are present. In the transfer of the current, practically only Na^+ and F^- ions take part.

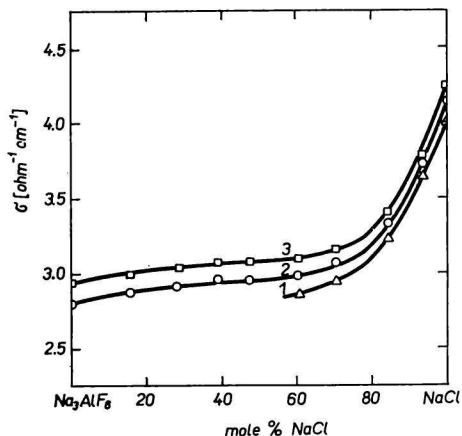


Fig. 1. Isotherms of the specific conductivity of molten binary Na_3AlF_6 — $NaCl$ mixtures.

1. 950°C; 2. 1000°C; 3. 1050°C.

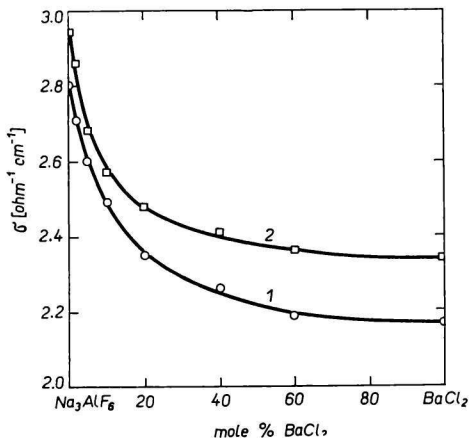


Fig. Isotherms of the specific conductivity of molten binary Na_3AlF_6 — $BaCl_2$ mixtures.

1. 1000°C; 2. 1050°C.

An addition of $NaCl$ introduces the mobile Na^+ and Cl^- ions into the melt; thus the increase of conductivity is not proportional to the increase of concentration of $NaCl$ since, owing to the increasing concentration of the Na^+ cations, the dissociation equilibrium of the reaction $Na^+F^- \rightleftharpoons Na^+ + F^-$ is shifted to the left. The suppression of the dissociation of the Na^+F^- ionic pairs affect most probably decisively the specific conductivity in the range of the inflection point at the conductivity isotherms. A rapid increase of the specific conductivity in the range of high $NaCl$ concentrations is effected by an increased concentration of the mobile Na^+ and Cl^- ions, whilst at the same time the concentration of the complex AlF_6^{3-} and AlF_4^- anions, participating in the current transfer in a negligible extent [20], is decreasing.

In the study of the specific electrical conductivity of the molten Na_3AlF_6 — $BaCl_2$ mixtures, the data concerning the maximum on the conductivity isotherms reported by *Belyaev* and co-workers [6, 8, 9] were not confirmed. From the course of the conductivity isotherms (Fig. 2) it follows that the course of the dependence $\sigma = f(c_{BaCl_2})$ is monotonous. In the concentration range 0—10 wt % $BaCl_2$ (approx. 0—10 mole % $BaCl_2$), the specific conductivity of the melt rapidly decreases with increasing concentration of barium chloride in the melt. The above-cited authors [6, 8, 9] assume that in the system Na_3AlF_6 — $BaCl_2$ at low concentrations of $BaCl_2$ the following reaction takes place



and, as a consequence of the increased concentration of Na^+ cations formed by dissociation of NaCl , the conductivity of the melt increases. With increasing concentration of BaCl_2 , the conductivity decreases owing to the formation of the complex AlF_6^{3-} anions.

Since no suitable data were available, it was not possible to calculate the change in free energy corresponding to the reaction (1); however, this reaction is highly improbable. In the cited works, no attempt was made to determine the reaction products, e.g. by means of the X-ray phase analysis, and the reaction (1) was compounded just in order to explain the existence of the experimentally determined maximum on the conductivity isotherms. Besides, even in the case that the reaction (1) occurs, it does not explain the increase in the conductivity of the melt. Both the starting substances (Na_3AlF_6 and BaCl_2) and the assumed reaction products (BaF_2 , NaCl , and AlF_3) are present in the melt evidently in the form of ions or of ionic pairs and not in a molecular form. Hence, regarding the structure of the melt, the composition of the starting and the resulting systems is identical. In both cases there are following ionic species in the melt: Na^+ and Ba^{2+} cations, F^- and Cl^- anions, the complex AlF_6^{3-} and AlF_4^- anions (which arise in the starting system as a result of the dissociation of cryolite, whereas in the final system they are formed by the association of AlF_3 and F^- anions which should arise by the dissociation of the hypothetical BaF_2), eventually also the ionic pairs Na^+F^- . The introduction of BaCl_2 into molten cryolite effects a decrease in the concentration of the Na^+ cations which take the major part in the transfer of current [20] as well as of the free F^- anions which evidently cannot be compensated by the presence of Ba^{2+} and Cl^- ions. The determined course of the isotherms of the specific conductivity appears to be in full agreement with the above analysis.

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