

Surface Tension and Density of Molten Fluorides and Fluoride Mixtures Containing Cryolite

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Using the Archimedean and pin detachment techniques, densities and surface tensions have been determined for the pure Alk.F (Alk. = Li, Na, K) with an accuracy better than $\pm 0.5\%$ and $\pm 1.5\%$, respectively, ($\rho_{\text{LiF}} = 1.746$, $\rho_{\text{NaF}} = 1.970$, $\rho_{\text{KF}} = 1.814 \text{ g cm}^{-3}$, and $\gamma_{\text{LiF}} = 216.6$, $\gamma_{\text{NaF}} = 183.5$ and $\gamma_{\text{KF}} = 129.2 \text{ mN m}^{-1}$ at 1000°C). The densities are in general 1% higher than previously reported data and the surface tensions are 2–4% lower.

The surface tension of molten Na_3AlF_6 is given by:

$$\gamma/\text{mN m}^{-1} = 273.74 - 1.38 \cdot 10^{-1} (T/^\circ\text{C})$$

For molten K_3AlF_6 the density and surface tension are given as temperature functions according to the equations:

$$\begin{aligned} \rho/\text{g cm}^{-3} &= 2.767 - 8.80 \cdot 10^{-4} (T/^\circ\text{C}) \\ \gamma/\text{mN m}^{-1} &= 208.63 - 1.08 \cdot 10^{-1} (T/^\circ\text{C}) \end{aligned}$$

The density of the Alk.F- AlF_3 systems has a maximum in the region of $x_{\text{AlF}_3} = 0.25$. This maximum is shifted to lower x_{AlF_3} with increasing temperatures.

The densities and surface tensions of the binary mixtures Na_3AlF_6 -LiF (NaF, KF, AlF_3 , K_3AlF_6 , Al_2O_3 , MgF_2 and CaF_2) and K_3AlF_6 -KF (AlF_3 , Al_2O_3) have been determined as functions of temperature and concentration. The observed variations in the surface tension are rationalized in terms of the ionic-covalent character of the melts.

The densities and surface tensions of the ternary mixtures Na_3AlF_6 -KF- Al_2O_3 , Na_3AlF_6 - AlF_3 - Al_2O_3 and Na_3AlF_6 - AlF_3 - CaF_2 have been determined as a function of temperature and concentration.

Numerical equations for the densities and surface tensions of the mixtures are given.

Both density and surface tension are important parameters in the technical electrolysis of aluminium. Substances which decrease electrolyte density may be beneficial as electrolyte additives for improving metal/melt separation during electrolysis.

In the aluminium electrolysis cell there are several interfaces at which surface forces appear and may be of importance: the interfacial tension between the electrolyte and the carbon influences the penetration of the electrolyte into the carbon lining, and the separation of carbon particles from electrolyte.¹

The interfacial tension between the aluminium and the electrolyte influences the rate of dissolution of metal in the electrolyte, which in turn affects the resulting current efficiency.² It also affects the coalescence of finely dispersed metal droplets in the electrolyte. Furthermore, the interfacial tension determines, in part, the ability of the interface to support undissolved alumina particles. This may

lead to the formation of alumina particles floating on top of the metal pad. This alumina will be in a far more favorable position for dissolution in the bath than the alumina present as a sludge between the metal pad and the carbon bottom. Moreover, in laboratory experiments³ and through theoretical calculations⁴ the current efficiency has been shown to increase in the presence of an alumina layer at the metal-bath interface.

The wetting of the anode by the electrolyte is a function of the interfacial tension at the three-phase region (gas/solid/liquid), and influences the gas bubble size, the interfacial anodic overvoltage and the onset of the anode effect.

The published surface tension data for cryolite melts^{5,6} are scarce and rather controversial. This work was initiated to remedy this situation and to allow quantitative conclusions to be drawn concerning the composition and temperature dependence of this property. Interfacial tension measurements in cryolite-Al systems obtained in our laboratory are being published.

The Archimedean technique and the pin (plane circular

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Table 1. Summary of systems investigated in this work.

One-component systems	
– NaCl	
– Alk.F (Alk. = Li, Na, K)	
– Alk. ₃ AlF ₆ (Alk. = Na, K)	
– Alk.AlF ₄ (Alk. = Na, K)	
Binary systems containing Na ₃ AlF ₆	
– NaF – AlF ₃	
– Na ₃ AlF ₆ – Al ₂ O ₃	
– Na ₃ AlF ₆ – LiF	
– Na ₃ AlF ₆ – KF	
– Na ₃ AlF ₆ – K ₃ AlF ₆	
– Na ₃ AlF ₆ – MgF ₂	
– Na ₃ AlF ₆ – CaF ₂	
Binary systems containing K ₃ AlF ₆	
– KF – AlF ₃	
– K ₃ AlF ₆ – Al ₂ O ₃	
Ternary systems containing Na ₃ AlF ₆	
– Na ₃ AlF ₆ – AlF ₃ – Al ₂ O ₃	
– Na ₃ AlF ₆ – AlF ₃ – CaF ₂	
– Na ₃ AlF ₆ – Al ₂ O ₃ – CaF ₂	
Quaternary systems containing Na ₃ AlF ₆	
– Na ₃ AlF ₆ – AlF ₃ – Al ₂ O ₃ – CaF ₂	

end-face) detachment technique were used for determination of density and surface tension, respectively. The choice of these methods was based on the following considerations:

- The corrosive nature of cryolite melts.
- Both methods are absolute and well-defined mathematically.
- Both methods may be combined to allow for the simultaneous determination of density and surface tension.
- Both methods are recommended by Janz⁷ as the most accurate techniques for measurement of these properties in molten salts.

Extensive reviews of techniques for determination of density^{8,9} and surface tension⁹ for molten salts have been published.

The systems and properties investigated in this work are presented in Table 1.

Experimental

Apparatus. The essential features of the thermobalance and the vacuum system have been described elsewhere,^{12,13} although the design has been somewhat altered as discussed by Bratland *et al.*¹⁴

Chemicals. All handling and storage of the salts was done in a glove box with a moisture content lower than 10 ppm. The chemicals used are listed in Table 2. Prior to use, the chemicals were purified by the following procedures:

Lithium, sodium and potassium fluoride were purified by the procedure used for sodium chloride.

Sodium chloride was recrystallized from the melt in a platinum crucible. The salt was dried at 300°C under vacuum for 3–4 h and was then melted at atmospheric pressure while passing a slow stream of nitrogen (~10 cm³ min⁻¹) through the furnace. The cooling rate was approximately 3–4°C h⁻¹. Only clear, transparent crystals were used.

Calcium fluoride and magnesium fluoride were dried overnight at 400°C under vacuum.

Aluminium trifluoride was sublimed twice in a vacuum furnace at 1000°C. The method has been described by Bratland.¹⁵ Frozen melts containing AlF₃ prepared by sublimation in graphite crucibles displayed a grayish surface colour, and the reproducibility of the surface tension measured in those melts was bad. This appears to be due to the presence of small particles of carbon from the graphite crucible in which the sublimation was performed. The carbon particles float on the cryolite-containing melts and hence become concentrated on the surface. A similar surface colour of the frozen melts was observed when the sublimation was carried out with boron nitride. The problem was overcome by using a synthetic corundum crucible covered by a platinum lid, where by the sublimed aluminium trifluoride was collected as a dense pad of well-defined crystals.

Table 2. Materials.

Compound	Grade	Supplier	Pretreatment
NaCl	<i>p.a.</i>	Merck AG, Darmstadt, FRG	Recrystallized
LiF	<i>p.a.</i>	Merck AG, Darmstadt, FRG	Recrystallized
NaF	<i>p.a.</i>	Merck AG, Darmstadt, FRG	Recrystallized
KF	<i>p.a.</i>	Merck AG, Darmstadt, FRG	Recrystallized
CaF ₂	<i>p.a.</i>	J. T. Baker Chemicals, Deventer, Netherlands	Dried at 400°C under vacuum
MgF ₂	<i>p.a.</i>	Semi-elements, Inc., USA	Dried at 400°C under vacuum
AlF ₃	Technical grade	Ardal og Sunndal Verk a.s., Norway	Sublimed at 1000°C under vacuum
γ-Al ₂ O ₃	<i>p.a.</i>	Merck AG, Darmstadt, FRG	Dried at 400°C under vacuum
Na ₃ AlF ₆	Handpicked	Kryolitselskabet Øresund, Copenhagen, Denmark	Dried at 200°C under vacuum
N ₂	99.99 %	Norsk Hydro, Herøya, Norway	None

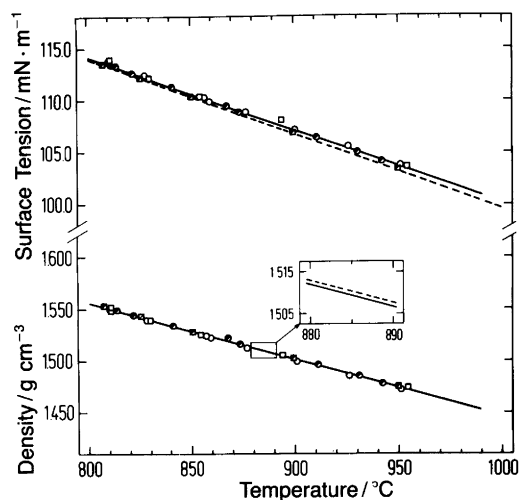


Fig. 1. Density and surface tension of molten NaCl. ●, ○, ■, □: this work (results from four runs); -----: Janz.⁷

Results

Precision and accuracy. Estimates of the precision were based on a least-squares statistical analysis of the data. The precision was taken as the value of the standard deviation expressed in per cent, and was $\pm 0.2\%$ for the density and $\pm 0.5\%$ for the surface tension data. The estimated experimental accuracies of the Archimedeian and the pin detachment methods are $\pm 0.5\%$ and $\pm 1.5\%$, respectively.⁷

Molten sodium chloride was used as reference to assess the accuracy of the measurements. The measured density and surface tension are given in Fig. 1, and they are compared in Fig. 2 with the recommended values^{7,11,16}, on a "per cent deviation" basis.

The per cent deviation is defined as:

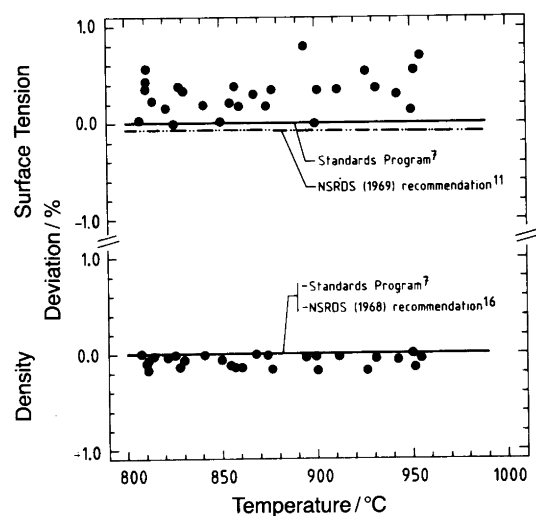


Fig. 2. Comparison of measured density and surface tension results for NaCl, with the data from the Standards Program and the NSRDS recommendations. ●: This work.

Per cent deviation =

$$\left[\frac{\text{measured value} - \text{recommended value}}{\text{recommended value}} \right] \cdot 100\%$$

Fig. 2 shows that the measurements agree well with the recommended values within the limits of accuracy of the experimental techniques used in this work.

One-component systems. The densities and surface tensions of the pure alkali fluorides LiF, NaF and KF were measured in the temperature range from the respective melting point to 1050, 1100°C. The experimental results are given by the equations

$$\rho/\text{g cm}^{-3} = a - b(T/^\circ\text{C}) \quad (1)$$

and

$$\gamma/\text{mN m}^{-1} = c - d(T/^\circ\text{C}) \quad (2)$$

respectively, and results are given in Table 3. The difference between the present results and those reported by Janz *et al.*¹⁶ is somewhat greater than the estimated accuracy of the present data.

Binary melts. 1. Density. The molar volumes of liquid mixtures are generally not additive. The deviation, known as the excess volume of mixing, for binary mixtures is defined through eqn. (3)

$$V^E = V_m - (x_1V_1^0 + x_2V_2^0) \quad (3)$$

In this equation V_m is the molar volume of the mixture, and V_i^0 and x_i are the molar volume and mole fraction, respectively, of component i . Excess molar volumes of binary melts may be expressed by equations of the type:¹⁷

$$V^E = x(1-x)(A + Bx + Cx^2 + Dx^3). \quad (4)$$

For the present binary melts the simplified equation

$$V^E = x(1-x)(A + Bx) \quad (5)$$

may be used. Using this equation the density of the binary melt may be expressed by

$$\rho_m = (x_1M_1 + x_2M_2) \{x_1V_1^0 + x_2V_2^0 + x(1-x)(A + Bx)\}^{-1} \quad (6)$$

where M_i is the molecular weight of component i . The temperature variation of the density is introduced through the parameters A and B .

$$A = A_1 + A_2(T - T_{\text{ref}})/^\circ\text{C} \quad (7)$$

$$B = B_1 + B_2(T - T_{\text{ref}})/^\circ\text{C}$$

Table 3. Coefficients in eqns. (1) and (2) giving the density (g cm^{-3}) and surface tension (mN m^{-1}), respectively, of LiF, NaF and KF.

Salt	Density, eqn. (1)		Surface tension, eqn. (2)	
	$a \pm \text{SD}$	$(b \pm \text{SD}) \cdot 10^5$	$c \pm \text{SD}$	$(d \pm \text{SD}) 10^3$
LiF	2.169 ± 0.015	42.3 ± 1.5	302.2 ± 1.4	85.5 ± 1.4
NaF	2.635 ± 0.001	66.5 ± 1.0	275.0 ± 1.2	91.5 ± 1.2
KF	2.503 ± 0.007	68.9 ± 0.8	213.3 ± 1.0	86.1 ± 1.1
Na_3AlF_6	3.097 ± 0.018	98.2 ± 1.7	273.7 ± 4.7	138.0 ± 0.4
NaAlF_4	2.294 ± 0.020	68.6 ± 2.1	112.1 ± 2.5	53.3 ± 2.6
K_3AlF_6	2.767 ± 0.020	88.0 ± 1.9	208.6 ± 5.3	108.0 ± 5
KAIF_4	2.231 ± 0.009	79.5 ± 1.1	100.8 ± 0.3	53.6 ± 0.4

where T_{ref} is an arbitrary reference temperature.

A combination of eqns. (6) and (7) turns out to fit the present experimental densities with sufficient accuracy. The results are given in Table 4. Isothermal densities at 1000°C plotted vs. composition are shown in Figs. 3 and 4.

2. *Surface tension.* Several models for surface tension of liquid mixtures have been published.^{18,19,20} None of these models will fit our experimental data due to the strong complexing tendencies in these melts.²¹ Using Na_3AlF_6 (K_3AlF_6) as one of the end members in all the binary systems containing NaF (KF), we obtain binary systems in which the major part of the complexation is already accounted for by the AlF_6^{3-} ion. It is then easier to construct a model equation that fits our data reasonably well.

Utigard²⁰ treated the liquid/gas interface as a separate phase. He assumed that it consisted of a single monolayer and that all the surface properties could be ascribed to it. According to Utigard the surface tension of a binary liquid mixture may be calculated using the equation:

$$\gamma_{12} = \frac{\theta\gamma_1\Gamma_1^{-1} + (1-\theta)\gamma_2\Gamma_2^{-1}}{\theta\Gamma_1^{-1} + (1-\theta)\Gamma_2^{-1}} \quad (8)$$

where

γ_{12} = surface tension of the mixture,

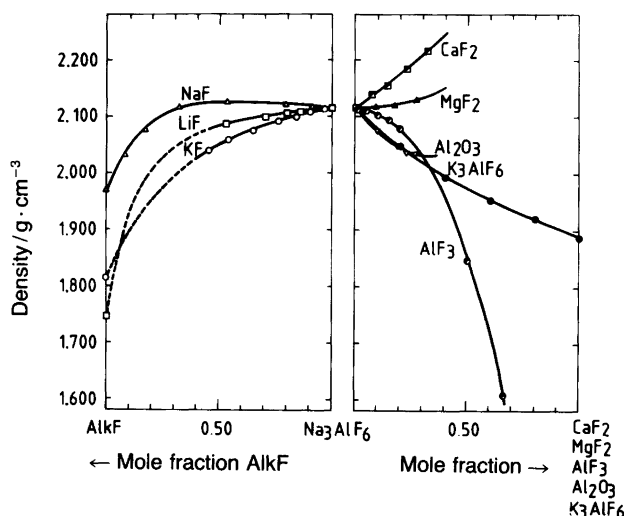


Fig. 3. Isothermal densities of $\text{Na}_3\text{AlF}_6\text{-MA}_x$ systems at 1000°C .

γ_i = surface tension of pure i ,

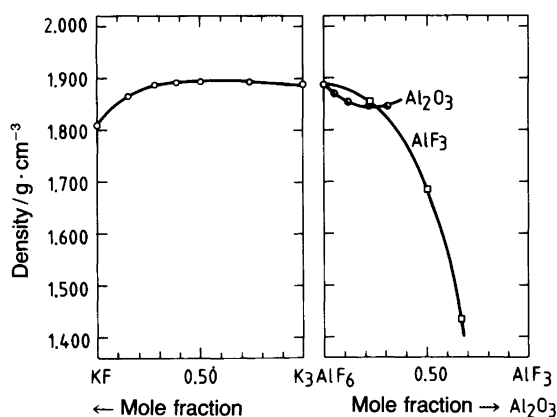
Γ_i = surface concentration of pure i , and

θ = fractional surface coverage of species 1

θ may be calculated from the standard Gibbs energy change, ΔG° , for the exchange reaction:

Table 4. Densities of some binary fluoride melts. Coefficients in eqns. (6) and (7). $T_{\text{ref}} = 1000^\circ\text{C}$.

System	A_1	$A_2 \cdot 10^3$	B_1	$B_2 \cdot 10^3$	Rel. SD/%
$\text{Na}_3\text{AlF}_6 - \text{LiF}$	$2.400 \cdot 10^{-1}$	6.323	-4.278	-9.538	0.05
$\text{Na}_3\text{AlF}_6 - \text{NaF}$	-3.447	2.771	-1.154	-10.42	0.15
$\text{Na}_3\text{AlF}_6 - \text{KF}$	$-7.358 \cdot 10^{-1}$	$-3.630 \cdot 10^{-4}$	$-5.142 \cdot 10^{-1}$	6.365	0.05
$\text{Na}_3\text{AlF}_6 - \text{Al}_2\text{O}_3$	34.130	-5.012	10.871	45.22	0.13
$\text{Na}_3\text{AlF}_6 - \text{MgF}_2$	4.720	-7.909	-1.092	-3.899	0.04
$\text{Na}_3\text{AlF}_6 - \text{K}_3\text{AlF}_6$	3.976	-2.094	-3.619	15.03	0.06
$\text{Na}_3\text{AlF}_6 - \text{CaF}_2$	-5.581	$-4.512 \cdot 10^{-1}$	1.610	8.405	0.07
$\text{Na}_3\text{AlF}_6 - \text{NaAlF}_4$	-18.333	15.65	-2.573	-67.77	0.09
$\text{K}_3\text{AlF}_6 - \text{KF}$	-2.100	5.950	-2.532	-7.360	0.06
$\text{K}_3\text{AlF}_6 - \text{Al}_2\text{O}_3$	46.477	$-26.29 \cdot 10^{-2}$	-18.389	98.44	0.13
$\text{K}_3\text{AlF}_6 - \text{KAIF}_4$	-19.039	$-5.835 \cdot 10^{-1}$	-23.188	34.17	0.02


 Fig. 4. Isothermal densities of $K_3AlF_6-MA_x$ systems at 1000°C.

$$1(\text{bulk}) + 2(\text{surface}) = 1(\text{surface}) + 2(\text{bulk}) \quad (9)$$

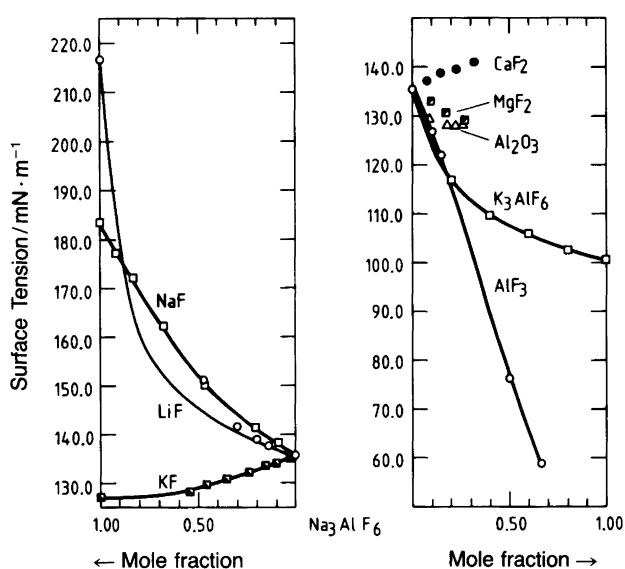
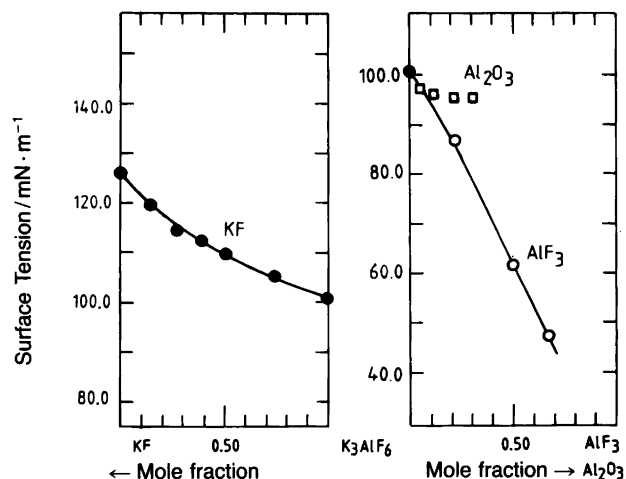
In the present case the above method is not useful, however, since the activity of an ionic component cannot be assumed to be proportional to the surface concentration of this component.

For numerical reasons we have curve-fitted the surface tension data using the equation

$$\gamma_{12} = \frac{x \gamma_1 \Gamma_1^{-1} + (1-x) \gamma_2 K \Gamma_2^{-1}}{x \Gamma_1^{-1} + (1-x) K \Gamma_2^{-1}} \quad (10)$$

in analogy with eqn. (8). In this equation K is an adjustable parameter, and x is the mole fraction of component 1 in the binary melt. For those systems for which the surface tension of the end members were known, this calculation may be performed.

In Figs. 5 and 6 the experimental binary surface tension


 Fig. 5. Isothermal surface tension of $Na_3AlF_6-MA_x$ systems at 1000°C. ●, ○, □, etc.: experimental data. —: eqn. (10).

 Fig. 6. Isothermal surface tension of $K_3AlF_6-MA_x$ systems at 1000°C. ●, ○, □: experimental data. —: eqn. (10).

data are compared with predictions of the model eqn. (10) at 1000°C. The temperature variation of γ was introduced using the equation:

$$\gamma_x(T) = \gamma_x(1000^\circ\text{C}) [\text{eqn. (10)}] + (a + bx + cx^2)(T - 1000)^\circ\text{C} \quad (11)$$

where x is the mole fraction of Na_3AlF_6 (K_3AlF_6) (in the binary containing both Na_3AlF_6 and K_3AlF_6 the mole fraction x refers to Na_3AlF_6).

Table 5 gives the coefficients in eqns. (10) and (11).

Multi-component systems. Density and surface tension data for some multi-component cryolite-containing melts are given in Table 6. The composition ranges covered are those of interest for the technical Hall-Héroult process for aluminium production.

Discussion

Density. 1. One component systems. The density data given in Table 3 for the pure alkali fluorides LiF, NaF and KF deviate from the reference data¹⁶ 0.7%, 1.4% and -0.2% at 1000°C for the above salts, respectively. These deviations are greater than the estimated accuracies of the pre-

Table 5. Coefficients in eqns. (10) and (11) for some binary cryolite-containing melts.

Binary system	K	$-a$	$-b$	c
Na_3AlF_6 - LiF	0.40	0.0855	0.1605	0.1080
- NaF	1.56	0.0913	0.1587	0.112
- KF	6.61	0.0861	0.1051	0.0532
- $NaAlF_4$	0.86	0.0461	0.1566	0.065
- K_3AlF_6	3.39	-0.108	-0.045	-0.075
K_3AlF_6 - KF	1.27	-0.0861	0.0747	0.0528
- $KAlF_4$	0.91	0.0488	0.0761	0.0166

Table 6. Density and surface tension in multicomponent cryolite melts of interest for the Hall-Héroult electrolysis. $\rho/\text{g cm}^{-3} = a - b(T/^\circ\text{C})$. $\gamma/\text{mN m}^{-1} = c - d(T/^\circ\text{C})$.

System: $\text{Na}_3\text{AlF}_6 - \text{AlF}_3 - \text{Al}_2\text{O}_3$.					
wt %		<i>a</i>	<i>b</i> · 10 ⁴	<i>c</i>	<i>d</i>
AlF_3	Al_2O_3				
4.9	2.0	3.008	9.36	222.9	0.102
4.8	4.0	2.945	8.90	199.9	0.0804
4.7	6.0	2.922	8.78	199.0	0.793
4.5	10.0	2.874	8.45	208.9	0.0877
9.8	2.0	2.950	9.12	198.2	0.0875
9.5	5.0	2.870	8.56	193.4	0.0824
9.0	10.0	2.789	7.91	205.2	0.0921

System: $\text{Na}_3\text{AlF}_6 - \text{CaF}_2 - \text{Al}_2\text{O}_3$.					
wt %		<i>a</i>	<i>b</i> · 10 ⁴	<i>c</i>	<i>d</i>
CaF_2	Al_2O_3				
4.9	2.0	3.030	9.18	247.3	0.114
4.75	5.0	2.966	8.70	236.7	0.105
4.50	10.0	2.880	8.11	225.5	0.0952
9.8	2.0	3.047	8.94	265.2	0.130
9.5	5.0	3.003	8.68	235.5	0.103
9.0	10.0	2.904	7.94	220.5	0.0895

System: $\text{Na}_3\text{AlF}_6 - \text{AlF}_3 - \text{CaF}_2 - \text{Al}_2\text{O}_3$.						
wt %			<i>a</i>	<i>b</i> · 10 ⁴	<i>c</i>	<i>d</i>
AlF_3	CaF_2	Al_2O_3				
1.96	1.96	0	3.120	9.77	264.4	0.131
1.88	5.89	0	3.135	9.79	270.0	0.135
1.80	9.82	0	3.160	9.83	273.3	0.137
5.89	1.88	0	3.080	9.70	253.4	0.128
5.66	5.66	0	3.115	9.75	258.2	0.131
5.43	9.46	0	3.155	9.86	260.3	0.132
9.82	1.80	0	3.041	9.50	243.6	0.127
9.46	5.43	0	3.094	9.70	249.5	0.130
9.06	9.09	0	3.139	9.83	254.2	0.134
4.9	4.9	2.0	3.057	9.51	234.7	0.110
4.75	4.75	5.0	2.974	8.90	222.9	0.0999
4.5	4.5	10.0	2.924	8.59	210.5	0.0877

sent results for LiF and NaF, and the reference data for these salts ought to be revised. The measured density data for Na_3AlF_6 agree within experimental error with values given by Grjotheim²², while data reported by Edwards *et al.*²³ are 1 % lower, probably due to the effect of the surface tension on the wire from which the sinker was suspended. This effect on the surface tension was not considered by Edwards. For K_3AlF_6 , no literature data are available.

2. *Binary and multicomponent systems.* Density isotherms for NaF- AlF_3 mixtures are presented in Fig. 7. They show the same general trend as reported previously.²²

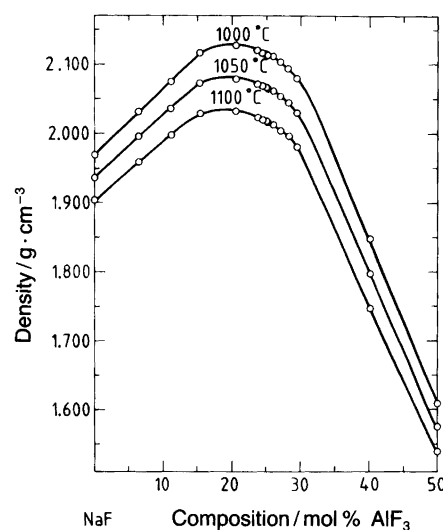
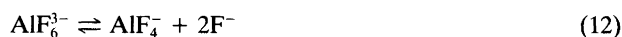


Fig. 7. Density isotherms for NaF- AlF_3 mixtures.

A maximum in the density appears in the composition range 15–25 mol % AlF_3 , and the position of this maximum shifts towards the NaF side as the temperature increases. The same effect has been observed²⁴ for the viscosity of NaF- AlF_3 mixtures.

On the basis of the dissociation model given by eqn. (12)



and the densities of pure liquid NaF and estimated values of the density of molten undissociated cryolite and molten NaAlF_4 , and assuming that the additivity rule can be applied to the molar volume of the ions present in the melt, Frank and Foster²⁵ have shown that the experimental densities could be fairly well described by the model when the degree of dissociation of cryolite, α , was 0.35 at 1000 °C.

Since the density of NaAlF_4 was measured in this work, the calculation was repeated; however, no reasonable value for the degree of dissociation of cryolite could account for the experimental data. The agreement between the experimental data and the model calculation given by Frank and Foster may be explained by the high value for the density of NaAlF_4 which was assumed, viz. 1.873 g cm^{-3} at 1000 °C (1.608 g cm^{-3} , this work). By assuming the cryolite melt to further contain the AlF_5^{2-} or $\text{Al}_2\text{F}_{10}^{4-}$ complex ions, which have been proposed to exist in these melts,²⁶ the model calculation can be made to fit the experimental data.

The existence of the AlF_5^{2-} or $\text{Al}_2\text{F}_{10}^{4-}$ ions has, however, not yet been observed experimentally, and we are therefore reluctant to base model calculations on the existence of these ions.

Since the simple ionic model of NaF- AlF_3 melts fail to describe the experimental density data, it does not seem reasonable to apply the same type of model to other mixtures containing cryolite.

A formalistic approach given by eqn. (5) was therefore applied to the quasi-binary systems containing cryolite, and

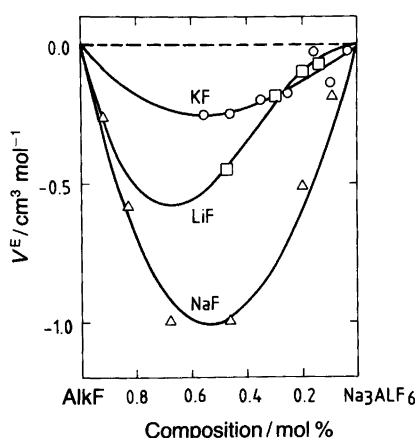


Fig. 8. Excess volume of mixing for Na_3AlF_6 -Alk.F mixtures at 1000°C . —: eqn. (5).

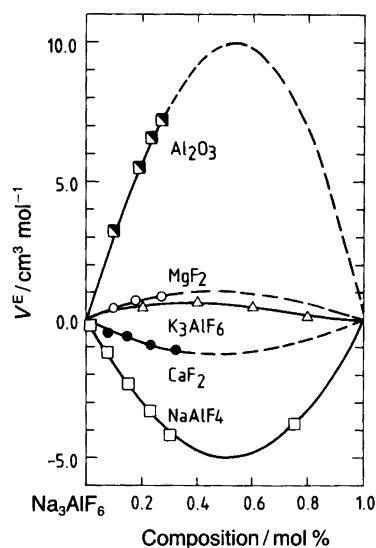


Fig. 9. Excess volume of mixing for Na_3AlF_6 - MA_x mixtures at 1000°C . —: eqn. (5).

the fitted excess volumes of mixing (Table 4) are presented in Figs. (8) and (9). As can be seen, both positive and negative excess volumes are observed. No obvious trend in the variation of these volumes with ionic potential, Z/r or ionic radii, r , of the additive is observed.

Density isotherms for KF-AlF_3 mixtures are presented in Fig. 10. They show the same general trend as the NaF-AlF_3 mixtures. A maximum is observed in the composition range 15–25 mol % AlF_3 , and the position of this maximum shifts towards the KF side as the temperature increases.

The excess volumes of mixing for the K_3AlF_6 - MA_x systems calculated from eqn. (5) and the coefficients A_{ij} and B_{ij} given in Table 4 are presented in Fig. 11. The trends are the same as observed for Na_3AlF_6 - MA_x mixtures. The variations observed for the densities which can be calculated from the data shown in Table 4 are closely related to the variations measured for the binary melts. Using the density data given in Tables 4 and 6 it should be relatively easy to

estimate the density of most technical melts with sufficient precision for industrial use.

Surface tension. 1. One component systems. As can be seen from Table 7, the discrepancies between the measured surface tension of the alkali fluorides and previous reference data are greater than the accuracy of the present measurements, as discussed previously. We thus conclude that the reference data should be revised.

Some of the surface tension data given in the literature

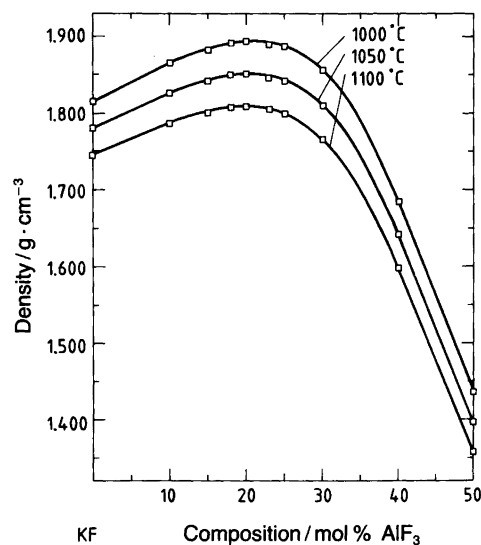


Fig. 10. Density isotherms for KF-AlF_3 mixtures.

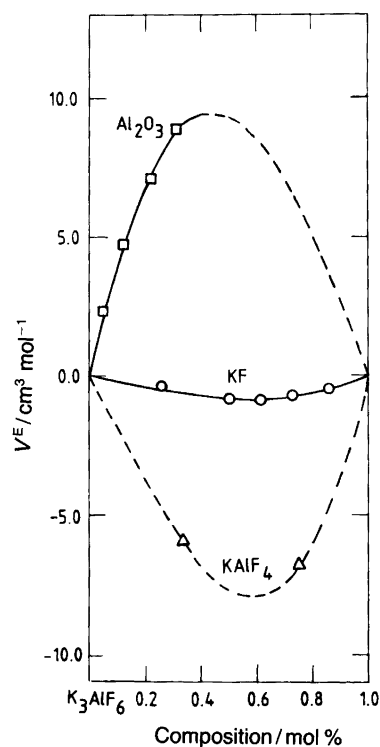


Fig. 11. Excess volume of mixing for K_3AlF_6 - MA_x mixtures at 1000°C . —: eqn. (5).

Table 7. Comparison of the measured surface tension (mN m^{-1}) of the alkali fluorides with previous reference data; $T = 1000^\circ\text{C}$.

Alk.F	Surface tension		
	This work	Ref. 11	Deviation / %
LiF	216.7	220.7	-1.8
NaF	183.5	185.2	-0.9
KF	127.2	132.1	-3.7

for Na_3AlF_6 ²⁷⁻³⁰ deviate by as much as 8% from the presented data. The data of Bratland *et al.*,¹⁴ and of Bloom and Burrows²⁸ are within the experimental error of the present work.

2. *Binary and multicomponent systems.* The isothermal surface tension of the two systems NaF- AlF_3 and KF- AlF_3 are presented in Figs. 12 and 13, respectively.

Both systems show the same variation of the surface tension as a function of the AlF_3 concentration. It appears that aluminium trifluoride is a surface-active component in the Alk.F- AlF_3 systems. This may be explained by the formation of AlF_6^{3-} and AlF_4^- complexes on adding AlF_3 to Alk.F. These ions have a stronger covalent character than the Alk.⁺ and F^- ions, and the covalent species will accord-

ingly concentrate on the surface of the melt to minimize the total Gibbs free energy of the system.

In the concentration range 15 to 35 mol% AlF_3 the change in surface tension per concentration unit of AlF_3 added is at its maximum. In this range the concentration of ions in the melts is mainly determined by the dissociation equilibrium of AlF_6^{3-} [eqn. (12)].

On adding AlF_3 to a basic but near neutral (Na_3AlF_6) melt, the concentration of AlF_4^- will increase drastically. Since the species AlF_4^- is much more covalent than AlF_6^{3-} , the change in covalent character of the melt for each concentration unit will be at its maximum at this concentration (Na_3AlF_6). This is why the variations in surface tension with x_{AlF_3} in the two systems NaF- AlF_3 and KF- AlF_3 resemble titration curves with "end points" at the M_3AlF_6 composition.

The isothermal surface tensions of the $\text{Na}_3(\text{K}_3)\text{AlF}_6\text{-MA}_x$ binary mixtures are presented in Figs. 5 and 6. Using the same qualitative arguments as in the preceding section one would expect to observe a reduction in the surface tension of cryolite when a salt with covalent character is added. This is indeed observed. The addition of AlF_3 and MgF_2 increases the concentration of AlF_4^- and thus the covalent nature of the melt. CaF_2 is certainly less able to capture F^- ions and to produce AlF_4^- than MgF_2 . Moreover, the Ca^{2+} ion has a field strength comparable to Li^+ and would accordingly be expected to increase the surface tension of cryolite. This is also observed. When Al_2O_3 dissolves in cryolite, large complexes are formed. These complexes have been discussed by Førlund and Ratkje,³¹ and by Sterten,³² and eqns. (13) and (14) give the probable reactions taking place when alumina dissolves in cryolite.

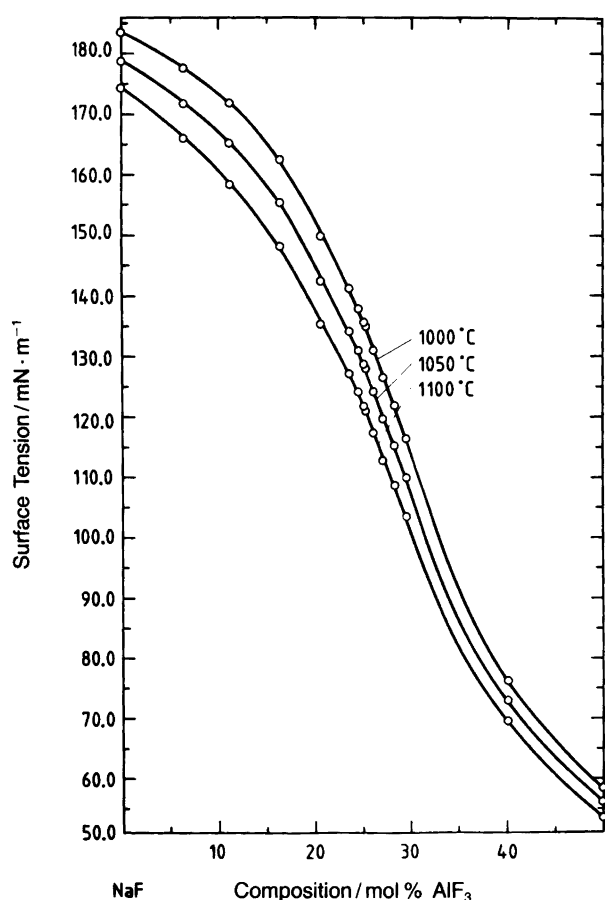


Fig. 12. Surface tension isotherms for NaF- AlF_3 mixtures.

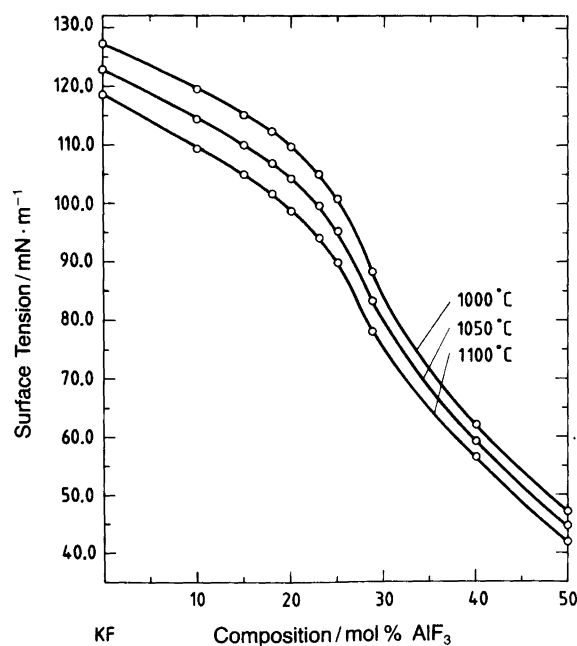
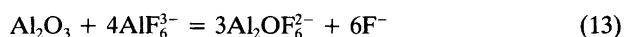
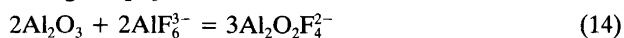


Fig. 13. Surface tension isotherms for KF- AlF_3 mixtures.

At low Al_2O_3 concentration:



At high Al_2O_3 concentration:



These complexes are covalent in nature relative to the cryolite melt and will concentrate in the surface and reduce the surface tension. The surface tension of pure Al_2O_3 is probably very much higher than that of cryolite (690 mN m^{-1} at 2050°C).³³ One should therefore expect an increase in surface tension at high alumina concentrations. Due to limited alumina solubility around 1000°C , however, we are not able to study the high alumina concentration region. A similar effect, however, may be observed in the Alk.F-cryolite systems. LiF and NaF, having much higher surface tensions than Na_3AlF_6 , increase the surface tension of the mixture when added to cryolite. This indicates that Na_3AlF_6 is surface active in these mixtures, as expected in view of the above arguments. Addition of KF, however, reduces the surface tension even though KF is clearly more ionic than Na_3AlF_6 . The reduction in surface tension in this case is due to the lower surface tension of pure KF than of Na_3AlF_6 .

The variations in the surface tension of K_3AlF_6 melts following the addition of AlF_3 , Al_2O_3 , KF and Na_3AlF_6 are as expected, the surface tension decreasing when AlF_3 and Al_2O_3 are added due to the formation of covalent complexes. The increase observed on adding cryolite may be explained by the higher surface tension of pure cryolite, and by the occurrence of minor structural changes when the Na and K salts are mixed.

The variations observed for the surface tensions which can be calculated from the data shown in Table 5 are closely related to the variations measured for the binary melts. Using the surface tension data given in Table 5 for the binary melts and those for multicomponent melts given in Table 6, it should be possible to estimate surface tension data for most melts of interest for Hall-Heroult electrolysis.

Conclusion

Available literature models for the density and surface tension of binary melts cannot satisfactorily explain our new experimental data for binary and quasi-binary melts containing Na_3AlF_6 (K_3AlF_6). The surface tension data may be rationalized qualitatively on the basis of acid-base or covalent-ionic properties of the melts.

The inverse S-shaped curves observed when the surface tension of binary NaF(KF)-AlF_3 melts is plotted versus mole fraction of AlF_3 are due to the AlF_6^{3-} dissociation reaction.

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