the observed elemental modification $4P_2$. To assist in its experimental identification, we have predicted its geometry, vibrational frequencies, and photoelectron spectrum. P_8 should also have a large electron affinity.

Acknowledgment. This work was supported by AFOSR Grant 82-0190. All computations were carried out on a VAX 11/750 minicomputer purchased with the aid of AFOSR Grant 84-0248. We acknowledge the assistance of Kim Baldridge with the statistical mechanical calculations. We thank Professor Jim Espenson for suggesting this interesting problem.

Note Added in Proof. Recent work by Raghavachari, Haddon, and Binkley[34] predicts the same order of stability $2P_4 > P_8 > 4P_2$ as our work. In addition, these workers established that the quantitative computation of the energy required for $P_4 \rightarrow 2P_2$ requires both a basis set containing f orbitals and at least third-order perturbation theory.

Registry No. P_8, 78998-14-8.

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Cryoscopy in the KCl–AlCl$_3$ System. High-Precision Phase Diagram near Equimolar Composition, with Comments on Oxide Contaminations and Effective Chloride Concentrations in Tetrachloroaluminate Melts

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The phase diagram of the KCl–AlCl$_3$ system near the equimolar composition is reported with high precision. The freezing point of the pure, congruently melting compound KAlCl$_4$ was determined to be 257.3 ± 0.1 °C. The molal freezing point depression constant of equimolar KCl–AlCl$_3$ melts was estimated to be 27 ± 2 °C kg mol^{-1}. The enthalpy of freezing for KAlCl$_4$ was found to be 18.0 ± 1.2 kJ mol^{-1}, in good agreement with the recently determined calorimetric value. The presence of oxide impurities in KCl–AlCl$_3$ melts was avoided by purifying the chemicals by fractionated recrystallization, and hence a phase diagram for melts essentially free of oxide impurities was obtained. The freezing point depression caused by deliberately added AlOCl showed dimerization, independent of the mole fraction in the range ~0.49 to ~0.52. Oxides dissolved in tetrachloroaluminate melts probably occur as $(AlOCl)_2(AlCl_4^-)_m$, $m = 1$ or 2, corresponding to solvation with one or two $AlCl_4^-$ species. The solubility has been cryoscopically determined to be ~0.08 and ~0.008 mol L^{-1} for NaCl and LiCl, respectively, in the KAlCl$_4$ melt at 257 °C, indicating $Na^+\cdots Cl^-$ and $Li^+\cdots Cl^-$ associations in this melt. The effective chloride concentration is approximately 10^2 times higher in KAlCl$_4$ than in NaAlCl$_4$ at the same mole fraction.

Introduction

Chloroaluminate melts have attracted considerable interest as general-purpose high-temperature ionic solvents, with low crystallization temperatures.

Previously, we considered the phase diagram of the NaCl–AlCl$_3$ system and found that it was inaccurately known in the vicinity of the equimolar mixture.[1]

The present work is a continuation study dedicated to the analogous KCl–AlCl$_3$ system. Detailed measurement of the phase diagram near the equimolar composition is reported, as is the molar freezing point depression constant for KAlCl$_4$ and its enthalpy and entropy of fusion. Further, the problem of oxide contaminations in tetrachloroaluminate melts is discussed.

Experimental Section

Chemicals. Because of the cryoscopic effect of impurities, very highly purified chemicals are needed for the determination of an accurate phase diagram. KCl (analytical reagent from Merck, >99.5% by weight) was purified (in a quartz apparatus) by first passing HCl gas over the solid and then through the melt (at ca. 850 °C), flushing with pure N$_2$, and finally filtering the melt. AlCl$_3$ was made and purified by distillation followed by recrystallization. LiCl, NaCl, CsCl, and CsBr of >99.5% purity were used after being dried at 150 °C for 2 days. AlOCl of >98.5% purity was prepared as previously described.[1] Especially purified KAlCl$_4$ was prepared by several fractionated recrystallizations, starting from a mixture of KCl and AlCl$_3$ with a slight excess of AlCl$_3$. After six recrystallizations the melting point remained constant at 257.30 ± 0.05 °C.

Technique. To prevent hydration of the chemicals, all manipulations were performed quickly in a dry N$_2$ glovebox. Chemicals were constantly stored under vacuum in sealed glass containers. Grinding to powders was avoided to keep moisture uptake at the lowest possible level. These precautions were necessary to obtain reproducible results.

Cryoscopic cells, the furnace, and other experimental details were described previously.[1] All temperatures were measured with the same 100-Ω platinum resistance thermometer system, which was calibrated to an absolute accuracy of ±0.1 °C (reproducibility on the order of 0.03 °C), by using ice water and 99.999 wt % pure Sn and Zn (231.97 and 419.58 °C).[2] The measured freezing points remained stable even after the melts were tempered for weeks.

Compositions are expressed in mole fractions, e.g. X_{AlCl_3} = mol of AlCl$_3$/(mol of AlCl$_3$ + mol of KCl). Oxides are not included in the mole fractions. Melts with X_{AlCl_3} >0.5, <0.5, and =0.5 are referred to as acidic, basic, and neutral, respectively.

Results and Discussion

KCl–AlCl$_3$ Phase Diagram. Before we report our own results, it is worth briefly mentioning previous results. The available information[3-11] is collected in Figure 1, which shows the consid-

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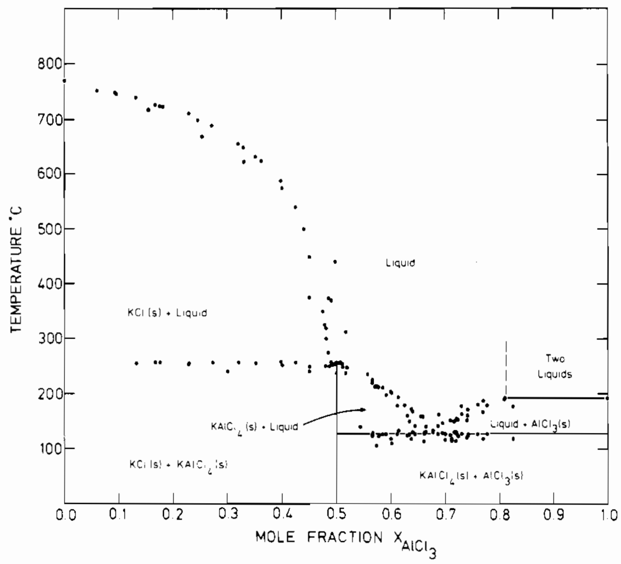

Figure 1. Phase diagram of the KCl–AlCl$_3$ system according to information in the literature.[3-11]

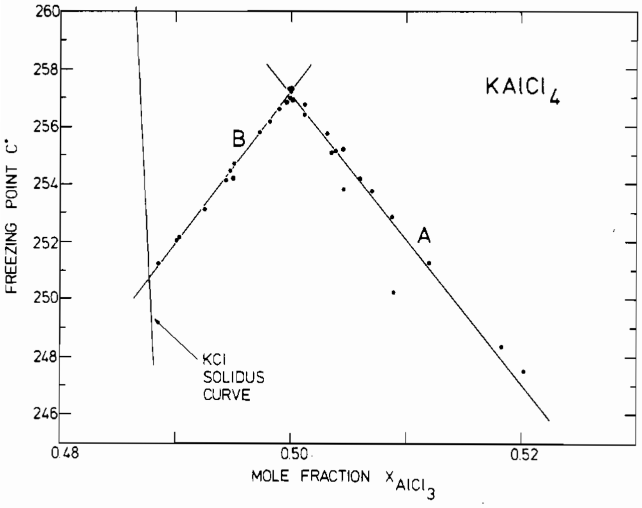

Figure 2. Observed phase diagram of the KCl–AlCl$_3$ system near the equimolar composition. The KCl solidus curve is calculated from the work of Brekke et al.[10] Also shown are the KAlCl$_4$ solidus regression lines A and B (cf. Table I).

erable scattering that exists among the literature results. This is probably due to varying levels of impurities (especially oxides), extensive tendency to subcooling without crystallization, and limited accuracies in the temperature determinations. Also, in the acidic range (e.g. near the eutectic at approximately $X_{AlCl_3} = 0.68$), evaporation of AlCl$_3$ into varying volumes might have changed the real melt compositions. The literature mentions melting points of KAlCl$_4$ in the range from 241 to 257 °C. The highest values are given in ref 5, 7, 8, and 11.

Our own measured freezing points for the KCl–AlCl$_3$ system as a function of composition are shown in Table I and Figure 2. The pure KAlCl$_4$ compound ($X_{AlCl_3} = 0.500$) melts congruently at 257.30 ± 0.05 °C.

It is interesting to note that the maximum freezing point occurs exactly at $X_{AlCl_3} = 0.50000$, independent of whether the starting chemicals were prepurified KAlCl$_4$ or mixtures of AlCl$_3$ and KCl. This was not the case in our previous study[1] on the NaCl–AlCl$_3$ system, where the value of 0.50045 was found and where corrections for the presence of oxide contaminations were needed. The reason for the more correct behavior obtained here is that the chemicals used now were of even better quality than before, due to the applied better method of purification of the AlCl$_3$ (new checks on the NaCl–AlCl$_3$ system showed that, with the purer AlCl$_3$, no oxide correction was necessary in that system either).

Table I. Observed Freezing Points T_f as a Function of the Mole Fractions X[a]

expt no.	mol of AlCl$_3$	mol of KCl	X_{AlCl_3}[d]	X_{KCl}[d]	T_f,[e] °C	line
A–0[b]	0.15647	0.15647	0.50000	0.50000	257.28	A + B
A–1[c]	0.16216	0.15647	0.50892	0.49108	250.23	A
A–2	0.16216	0.15924	0.50454	0.49546	253.81	A
A–3	0.16216	0.16139	0.50118	0.49882	256.43	A
A–4	0.16216	0.16221	0.49992	0.50008	257.00	B
B–0[b]	0.15206	0.15206	0.50000	0.50000	257.28	A + B
B–1	0.15206	0.15317	0.49818	0.50182	256.18	B
B–2	0.15206	0.15552	0.49438	0.50562	254.14	B
B–3	0.15206	0.15806	0.49033	0.50967	252.15	B
B–4	0.16054	0.15806	0.50389	0.49611	255.16	A
B–5	0.16372	0.15806	0.50879	0.49121	252.87	A
B–6	0.16372	0.16292	0.50122	0.49878	256.78	A
C–0[b]	0.14152	0.14152	0.50000	0.50000	257.24	A + B
C–1	0.14152	0.14305	0.49731	0.50269	255.81	B
C–2	0.14152	0.14583	0.49251	0.50749	253.12	B
C–3	0.14152	0.14819	0.48849	0.51151	251.23	B
D–0[b]	0.11835	0.11835	0.50000	0.50000	257.24	A + B
E–0	0.22916	0.22929	0.49986	0.50014	257.31	B
E–1	0.23255	0.22929	0.50353	0.49647	255.10	A
E–2	0.23582	0.22929	0.50702	0.49298	253.75	A
E–3	0.24056	0.22929	0.51199	0.48801	251.26	A
F–0	0.20697	0.20781	0.49898	0.50102	256.62	B
F–1	0.20697	0.21138	0.49473	0.50527	254.48	B
G–0	0.08510	0.07848	0.52021	0.47979	247.51	A
G–1	0.08510	0.07909	0.51828	0.48172	248.36	A
H–0[b]	0.09122	0.09122	0.50000	0.50000	257.25	A + B
H–1	0.09122	0.09302	0.49509	0.50491	254.73	B
I–0[b]	0.06572	0.06572	0.50000	0.50000	257.28	A + B
I–1	0.06572	0.06838	0.49010	0.50990	252.04	B
J–0[b]	0.06921	0.06921	0.50000	0.50000	257.31	A + B
J–1	0.07008	0.06921	0.50315	0.49685	255.76	A
K–0[b]	0.07600	0.07600	0.50000	0.50000	257.23	A + B
L–0[b]	0.06771	0.06771	0.50000	0.50000	257.34	A + B
M–0	0.10194	0.10410	0.49477	0.50523	254.23	B
N–0	0.09418	0.09253	0.50440	0.49560	255.20	A
O–0	0.09519	0.09529	0.49975	0.50025	256.90	B
P–0	0.08078	0.08078	0.50001	0.49998	256.98	A
Q–0	1.05017	1.02507	0.50605	0.49395	254.20	A
R–0	0.06223	0.06223	0.50000	0.50000	257.12	A + B

[a] The data fit two lines. Least-squares regression by $T_f = \alpha + \beta \times (X_{AlCl_3} - 0.5)$ with T_f in °C. Regression line A: $\alpha = 257.11 \pm 0.15$ °C, $\beta = -502 \pm 22$ °C, $R^2 = 0.9605$. Regression line B, $\alpha = 257.22 \pm 0.03$ °C, $\beta = 529.6 \pm 6$ °C, $R^2 = 0.9972$. [b] Starting from recrystallized KAlCl$_4$. [c] I.e. cell A with addition no. 1. [d] Accuracy ±0.00003. [e] Precision ±0.05.

The presence of a sharp (not rounded) peak of the liquidus curve at $X_{AlCl_3} = 0.5$ indicates that the complex AlCl$_4^-$ does not self-dissociate appreciably into Al$_2$Cl$_7^-$ and Cl$^-$.

In Figure 2, the KCl liquidus curve (i.e. the solubility of solid KCl in molten KCl–AlCl$_3$ expressed as X_{AlCl_3} vs. temperature) was obtained by calculation as described previously,[1] from potentiometrically determined solubility data given by Brekke et al.[10] and the density of the melt.[12,13] An equivalent liquidus line could be obtained by Dewing's method[14] of fitting expression 1 to the

$$\log (0.5 - X_{AlCl_3}) = A - B/T \qquad (1)$$

known points[7,9-10] on the KCl liquidus curve at higher temperatures, and extrapolating the expression into the range of interest here. (A and B are parameters, $A \simeq 0.148$ and $B \simeq 1080$; T is absolute temperature.)

As it can be seen from Figure 2, the eutectic between KCl and KAlCl$_4$ occurs at ca. 250.8 °C for $X_{AlCl_3} = 0.4877$. The estimated precision of this eutectic point is better than ±0.3 °C for the temperature and ±0.0001 for the composition. This result is in excellent agreement with the position at 250 °C and 0.490 found by Fischer and Simon[7] (see also ref 9). Readers of phase diagram

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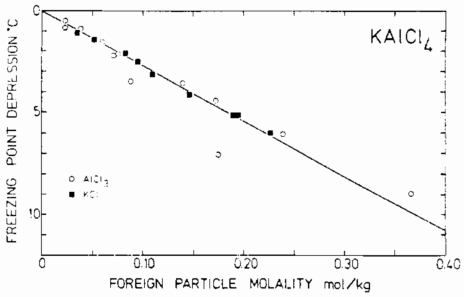

Figure 3. Freezing point depression θ for KAlCl$_4$ vs. molality m of added foreign substances of AlCl$_3$ and KCl. The regression line through the origin corresponds to $\lambda = 27$.

collections are warned that diagrams recently published[15,16] for the KCl–AlCl$_3$ system show neither the eutectic between KCl and KAlCl$_4$ nor the congruent melting point of KAlCl$_4$, even though most of the data showing this behavior were published more than 20 years ago.

Determination of the Molal Freezing Point Depression Constant, λ. The freezing point depression of a solvent (i.e. KAlCl$_4$) to which substances (solutes) are added in small quantities can be expressed by the limiting Raoult–van't Hoff relation:

$$\theta \simeq \nu\lambda m \simeq \nu\frac{M}{1000}\left(\frac{RT_f^2}{\Delta H_f}\right)m \qquad (2)$$

Here, θ is the freezing point depression (°C), ν is the number of foreign particles formed in the melt per mole of the added substance, m is the molality (mol/kg of solvent) of the added substance, R is the gas constant (8.3144 J mol^{-1} K^{-1}), and ΔH_f, M, and T_f are the enthalpy of fusion (J mol^{-1}), the molar weight (g mol^{-1}), and the freezing point (K) of the pure solvent.

The freezing point depression constant of the solvent KAlCl$_4$ can be estimated from our data in Table I. Useful combinations of experiments and corresponding calculations are shown in Table II, and obtained values of m and θ are plotted in Figure 3. There is agreement between the points obtained from AlCl$_3$ and KCl addition experiments. It is reasonable to assume that both AlCl$_3$ and KCl form (or consume) one particle (Al$_2$Cl$_7^-$ and Cl$^-$) when added to KAlCl$_4$ melts. The K$^+$ ions from the dissociation of KCl are common to the solvent (consisting of K$^+$ and AlCl$_4^-$) and are cryoscopically inactive.[17] The assumption that both AlCl$_3$ and KCl are cryoscopically active with $\nu = 1$ is in accordance with calorimetric results (see below). The limiting freezing point depression constant λ can then be obtained from eq 2. Ideally, the slope of the curve in a plot like Figure 3 should be evaluated at $m = 0$. This extrapolation is difficult because of the large relative scattering at small m. Linear regression of the θ vs. m data in Table II gives a line with a slope of 25 ± 2 °C kg mol^{-1} or, if forced through the origin, a slope of 27 ± 1 °C kg mol^{-1}, but these slopes are much influenced by the θ values at high m. On the other hand, linear regression of the θ/m vs. m data has an intercept of 29 ± 2 °C kg mol^{-1} (the θ/m average is 28.28 °C kg mol^{-1}). The conclusion is that λ can be estimated to be 27 ± 2 °C kg mol^{-1}.

Enthalpy and Entropy of Fusion of KAlCl$_4$. The λ value may be used to obtain the enthalpy of fusion ΔH_f at the melting point (530.45 K, 257.3 °C) from eq 2. The result is 18.0 ± 1.2 kJ mol^{-1}. A comparison with calorimetric values in the literature is quite interesting. The value of 10.5 kJ mol^{-1} reported by Godun et al.[18] is probably erroneous. A recent paper by Denielou et al.[19] reports a higher value of 19.3 ± 0.6 kJ mol^{-1}. This value is probably correct within ±2.0 kJ mol^{-1}, according to arguments given previously,[1] and hence is in reasonable accordance with our cryoscopically determined value. On the other hand, our value is slightly lower than theirs (as for NaAlCl$_4$) so there is room for a premelting effect, although smaller than what was found for NaAlCl$_4$. However, since the crystal structures of NaAlCl$_4$ and KAlCl$_4$ are much different,[20] we do not need to find a premelting effect here.

Table II. Experiments Used for Estimation of the Limiting Freezing Point Depression Constant

ref expt	obsvn expt	addn,[a] mmol	molality increment, m	depression θ,[b] °C	slope θ/m, °C kg/mol
A-0	A-1	5.69	0.174 72 (AlCl$_3$)	7.05	40.30
A-0	A-2	2.92	0.083 20 (AlCl$_3$)	3.47	39.34
A-0	A-3	0.77	0.022 95 (AlCl$_3$)	0.85	37.04
B-0	B-4	2.48	0.075 47 (AlCl$_3$)	2.12	28.09
B-0	B-5	5.66	0.172 25 (AlCl$_3$)	4.41	25.60
B-0	B-6	0.80	0.023 62 (AlCl$_3$)	0.50	21.17
E-0	E-1	3.39	0.071 16 (AlCl$_3$)	2.21	31.06
E-0	E-2	6.66	0.139 79 (AlCl$_3$)	3.56	25.47
E-0	E-3	11.40	0.239 29 (AlCl$_3$)	6.05	25.28
H-0	G-1	6.01	0.365 52 (AlCl$_3$)	8.89	24.32
G-1	G-0	0.66	0.038 36 (AlCl$_3$)	0.85	22.16
J-0	J-1	0.87	0.060 47 (AlCl$_3$)	1.55	25.63
B-0	B-1	1.11	0.035 11 (KCl)	1.10	31.33
B-0	B-2	3.46	0.109 45 (KCl)	3.14	28.69
B-0	B-3	6.00	0.189 80 (KCl)	5.13	27.03
C-0	C-1	1.53	0.052 00 (KCl)	1.43	27.50
C-0	C-2	4.31	0.146 49 (KCl)	4.12	28.12
C-0	C-3	6.67	0.226 71 (KCl)	6.01	26.51
F-0	F-1	3.57	0.082 85 (KCl)	2.14	25.83
H-0	H-1	1.80	0.094 92 (KCl)	2.52	26.55
I-0	I-1	2.66	0.194 69 (KCl)	5.24	26.91
					av 28.28

[a] The relative increment in AlCl$_3$ or KCl is calculated from Table I. [b] Freezing point depression from reference to observation experiment; see Table I.

The entropy of fusion (ΔS_f) of KAlCl$_4$ is 33.9 J mol^{-1} K^{-1} calculated as $\Delta H_f/T_f$ (for NaAlCl$_4$ it was 36.1 J mol^{-1} K^{-1}). This is a reasonable magnitude.[17]

Other Thermodynamic Data. The KCl–AlCl$_3$ system has been the subject of various phase diagram calculations,[21–23] as has the NaCl–AlCl$_3$ system. Thermodynamic data (excess molar free energy) of acidic[21] and basic[22,23] KCl–AlCl$_3$ melts have been obtained and compared with results originating from EMF[10,24–26] and vapor pressure[10,22,27,28] measurements. From the thermodynamic data the phase diagram has been reproduced[21–23] with a precision on the order of 1–10 °C. Now that the phase diagram is known much more precisely, better thermodynamic data should be attainable.

General Data. It is well-known that oxide impurities, originating from moisture or vessel corrosion, are very difficult to avoid in tetrachloroaluminate melts.[29] As discussed previously,[1] the be-

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Table III. Determination of the Cryoscopic Effect of AlOCl on KAlCl$_4$

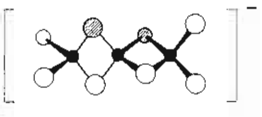
expts		mol of AlCl$_3$	mol of KCl	$X_{\mathrm{AlCl_3}}{}^{a,c}$	T_f,^{a,d} °C	mmol of added AlOCl	molality increment, m_{AlOCl}	T_f,^{d} °C	θ, °C	$\nu_{\mathrm{AlOCl}}{}^{b,e}$
C-3	C-4	0.141 52	0.148 19	0.488 49	251.23	0.841 47	0.0281	250.78	0.45	0.59
D-0	D-1	0.118 35	0.118 35	0.500 00	257.24	0.658 52	0.0268	256.93	0.31	0.43
E-3	E-4	0.240 56	0.229 29	0.511 99	251.26	1.325 96	0.0270	250.97	0.29	0.40
F-1	F-2	0.206 97	0.211 38	0.494 73	254.48	1.141 09	0.0263	254.22	0.26	0.37
G-1	G-2	0.085 10	0.079 09	0.518 28	248.36	0.474 28	0.0275	248.00	0.36	0.48
H-1	H-2	0.091 22	0.093 02	0.495 09	254.73	0.511 26	0.0268	254.54	0.19	0.26
I-1	I-2	0.065 72	0.068 38	0.490 10	252.04	0.418 19	0.0302	251.83	0.21	0.26
J-1	J-2	0.070 08	0.069 21	0.503 15	255.76	0.418 19	0.0288	255.53	0.23	0.30
K-0	K-1	0.076 00	0.076 00	0.500 00	257.23	0.429 66	0.0272	256.76	0.47	0.64

[a] Before addition of AlOCl. [b] ν = number of foreign particles formed per AlOCl added = $\theta/(\lambda m_{\mathrm{AlOCl}})$; λ = 27 °C kg mol^{-1}. [c] Accuracy ±0.000 05. [d] Precision ±0.05. [e] Accuracy ±0.2.

havior of oxide ions in the melts has been the subject of much confusion. However, it is now commonly agreed that no free oxide ion "O^{2-}" is present. Instead, oxide reacts with the melt according to the reaction

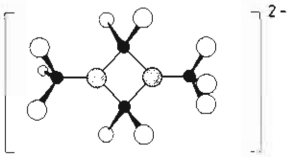
$$\text{"O}^{2-}\text{"} + \mathrm{AlCl_4^-} \rightarrow \text{"AlOCl"} + 3\mathrm{Cl^-} \qquad (3)$$

The exact chemical formulas of the solutes designated "AlOCl" are not known. In our previous study[1] on oxides in NaAlCl$_4$ melts, we indicated for "AlOCl" dimeric solvated species like (AlOCl)$_2$(AlCl$_4^-$)$_m$. For m = 1, a simple, structurally satisfactory molecular ion can be formulated (I), which fulfills the requirement of tetrahedral coordination around aluminum. Another satisfactory possibility, discovered on the basis of recently established[30,31] crystal structures of two [Al$_4$Cl$_{10}$O$_2$]$^{2-}$ salts, is the molecular ion II, corresponding to m = 2 in the formula (AlOCl)$_2$(AlCl$_4^-$)$_m$.



$\mathrm{Al_3O_2Cl_6^-}$

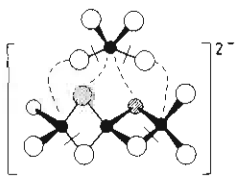
I



$\mathrm{Al_4O_2Cl_{10}^{2-}}$

II

Ions I and II can be regarded as closely related via acceptance/rejection of one solvent AlCl$_4^-$ ion as shown in III. "AlOCl" can be considered as a chloroamphoteric substance (see eq 4), but the evidence for this behavior is not yet conclusive.



$\mathrm{AlCl_4^- \cdot Al_3O_2Cl_6^-}$

III

$$\text{"AlO}^{+}\text{"} + 2\mathrm{Cl^-} \rightleftarrows \text{"AlOCl"} + \mathrm{Cl^-} \rightleftarrows \text{"AlOCl}_2^{-}\text{"} \qquad (4)$$

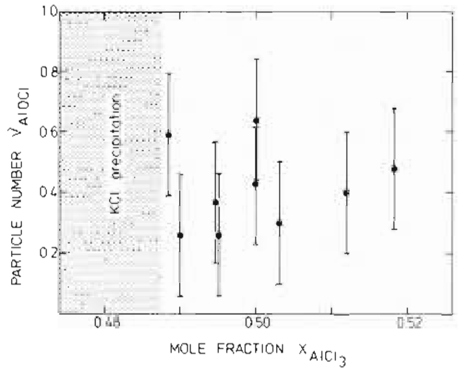
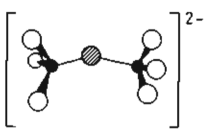


Figure 4. Number of foreign particles formed per added AlOCl particle vs. composition.

Support for the existence of "AlOCl$_2^-$" comes indirectly. Recently, a salt of composition (NO)$_2$[Al$_2$OCl$_6$] (see IV) was prepared (from AlCl$_3$ and CCl$_3$NO$_2$ in CH$_2$Cl$_2$ solution) and characterized by chemical analysis and IR spectroscopy,[32] and also Cs$_2$[Al$_2$OCl$_6$] seems to exist in the solid state.[33] Other oxychloroaluminates, like KAlOCl$_2$,[34] K[Al$_4$O$_4$Cl$_5$],[35] and K$_m$-(Al$_3$O$_4$Cl)$_n$(AlCl$_4^-$)$_m$,[36] have been found in the past, indicating that "AlOCl" is able to associate further chloride ions under certain circumstances. "AlOCl$_2^-$" and the well-known "AlO$_2^-$" ion are equivalent forms except for solvation, as can be seen from eq 5.

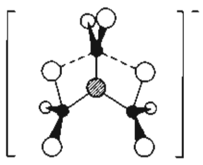


$\mathrm{Al_2OCl_6^{2-}}$

IV

$$2\mathrm{AlOCl_2^-} \rightleftarrows \mathrm{AlO_2^-} + \mathrm{AlCl_4^-} \qquad (5)$$

Regarding evidence for the existence of "AlO$^+$", the ion [Al$_3$OCl$_8$]$^-$ (see V) was found in a metalloorganic chromium salt and char-



$\mathrm{Al_3OCl_8^-}$

V

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Table IV. Determination of the Cryoscopic Effect of Various Alkali-Metal Halides on $KAlCl_4$

expts		X_{AlCl_3}[a]	mmol of added MX	molality increment, *m*	depression θ, °C
S-0	S-1	~0.4992[b]	0.59	0.050 (LiCl)	0.16[c]
T-0	T-1	~0.4990[b]	0.27	0.025 (LiCl)	0.25[c]
L-0	L-1	0.50000	0.89	0.0636 (NaCl)	2.52[c]
L-0	L-2	0.50000	1.60	0.1134 (NaCl)	2.64[c]
P-0	P-1	0.50001	0.39	0.0230 (NaCl)	1.19
P-0	P-2	0.50001	0.86	0.0510 (NaCl)	2.36
P-0	P-3	0.50001	1.60	0.0955 (NaCl)	2.50[c]
P-0	P-4	0.50001	3.12	0.1856 (NaCl)	2.53[c]
R-0	R-1	0.50000	0.52	0.0400 (CsCl)	0.64
R-0	R-2	0.50000	3.12	0.2413 (CsCl)	1.10
A-4	A-5	0.49992	0.43	0.0128 (CsBr)	0.35
A-4	A-6	0.49992	1.95	0.0579 (CsBr)	1.18

[a] For solvent only (both experiments). [b] Cell contained ~11.5 g of $KAlCl_4$ of approximately the composition indicated. [c] Precipitate observed.

acterized by an X-ray structure determination.[30] This ion can be considered to be a disolvated "AlO^+" ion, i.e. $(AlO^+)(AlCl_4^-)_2$.

The chloroamphoteric behavior (eq 4) of "AlOCl" has recently been further confirmed in our laboratory, in basic $CsCl-AlCl_3$ melts by means of vibrational spectroscopy[37] and in acidic $NaCl-AlCl_3$ melts by means of potentiometry.[38] It must however be stated that in nearly neutral melts the neutral "AlOCl" has a considerable pCl range of stability.[39]

Cryoscopic Experiments with AlOCl Dissolved in $KAlCl_4$. It is known[36] that AlOCl has a certain (small) solubility in equimolar $KAlCl_4$. To investigate the behavior of oxide in the $KCl-AlCl_3$ system, small quantities of AlOCl were deliberately added to melts of known composition and with known freezing points. After equilibration, resulting in complete solubilization of the oxide, the freezing points were measured to determine the cryoscopic effect of AlOCl. The results shown in Table III and in Figure 4 can be summarized in this way.

The number of particles formed per added AlOCl formula (i.e. ν_{AlOCl}) is 0.4 ± 0.2, independent of the composition of the $KCl-AlCl_3$ melt within the range studied here. This is a result completely analogous to the $NaCl-AlCl_3$ case,[1] except that the examined range now is broader. As discussed previously,[1] the ν_{AlOCl} value of ~0.5 means that two virgin AlOCl particles on the average are needed to form one cryoscopically active particle. Virgin unsolvated AlOCl or solvated particles like $(AlOCl)(AlCl_4^-)$ or $(AlOCl)(AlCl_4^-)_2$, which require $\nu_{AlOCl} = 1.0$, can thus be excluded in the investigated range. The most reasonable explanation for the $\nu \sim 0.5$ result is the occurrence of $(AlOCl)_2(AlCl_4^-)_m$ ions of the kind I or II or isomers of these, but it must be admitted that other possibilities exist.

Other Cryoscopic Results for $KAlCl_4$ Melts

It was found of interest also to study the cryoscopic behavior of other alkali-metal halides when added to $KAlCl_4$ melts. The experiments are summarized in Table IV and in Figure 5.

It is seen that additions of CsCl and CsBr give a nonlinear cryoscopic dependence, and much fewer particles are formed than what is expected. A likely explanation may be that these compounds form solid solutions with $KAlCl_4$. Analogously, for additions of $FeCl_3$ to $NaAlCl_4$ we have observed[40] a value of ν around zero and the simultaneous formation of uniformly yellow crystals, indicating solid solubility of $FeCl_4^-$ in $NaAlCl_4$. Similarly, $AlBr_3$ added to neutral $NaAlCl_4$ gave a value[40] for ν_{AlBr_3} of around 1.5, indicating that the four particles formed[41] by rearrangement reactions ($3AlCl_3Br^- + AlCl_3$) seem to dissolve substantially in the $NaAlCl_4$ crystals.

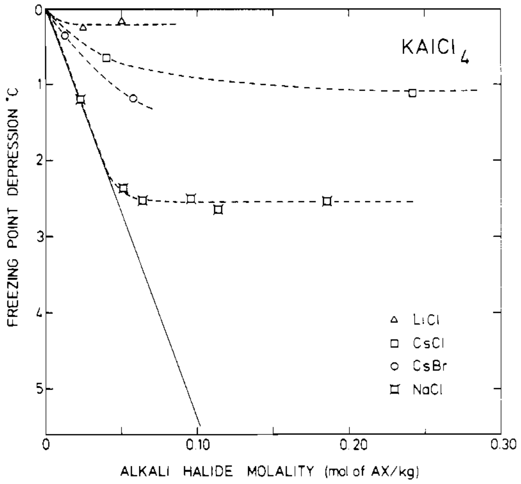

Figure 5. Freezing point depression θ for $KAlCl_4$ vs. molality *m* of added foreign substances for LiCl, NaCl, CsCl, and CsBr. Dashed curves represent estimated dependences, and the line is the expected dependence for a salt AX forming two foreign particles.

Previously,[1] we have added CsBr to $NaAlCl_4$ and found a ν_{CsBr} value of 2. This was interpreted[1] as the formation of Cs^+ and Br^- particles, but according to later experience[41] the Br^- particle probably gives rise to Cl^- and $AlCl_3Br^-$ particles by reaction with the solvent. The incorporation of $AlCl_3Br^-$ into the $KAlCl_4$ crystals then could explain the observed deviation from $\nu = 3$. (That ν accidently came out as 2 is a feature which shows the kind of caution one always has to exercise when cryoscopic data are interpreted.)

From the occurrence of a horizontal level on the sodium chloride curve in Figure 5, and from the visual observation of a precipitate at large *m*, it seems as if NaCl at about 257 °C has a limited solubility on the order of 0.050 mol kg^{-1} of $KAlCl_4$ melt. At this temperature, the density[13] of the solvent is ca. 1.647 g cm^{-3}, from which a solubility on the order of 0.082 mol of NaCl/L of $KAlCl_4$ melt is obtained.

The NaCl molar solubility product is defined in eq 6, where $[Na^+]$ and $[Cl^-]$ are the concentrations of the respective ions in mol L^{-1}. From the obtained solubility, a molar solubility product, K_s, of 0.00678 $mol^2\ L^{-2}$ can be determined.

$$K_s = [Na^+][Cl^-] \qquad (6)$$

Similarly, for LiCl in $KAlCl_4$ at ~257 °C a limited solubility on the order of 0.005 mol kg^{-1} or ca. 0.008 mol L^{-1} can be estimated, from the data in Table IV and Figure 5.

If one extrapolates/interpolates data from previous potentiometric work,[10,42] the molar solubility constants, K_s, for the solubility of KCl in $KAlCl_4$ and NaCl in $NaAlCl_4$ at the same temperature, ~257 °C, can be calculated. The results obtained are shown in Table V.

The higher K_s value of 3.22 $mol^2\ L^{-2}$ for KCl saturation relative to 0.00678 $mol^2\ L^{-2}$ for NaCl saturation and relative to 0.00064 $mol^2\ L^{-2}$ for LiCl saturation in molten $KAlCl_4$ at ~257 °C is of course not remarkable because of the difference between the K^+, Na^+, and Li^+ ions and their respective chloride crystals.

Perhaps more interestingly, the K_s product for NaCl saturation at ~257 °C goes from 1.46 $mol^2\ L^{-2}$ in $NaAlCl_4$ to 0.00678 $mol^2\ L^{-2}$ in $KAlCl_4$ melts. The ratio $K_s(\text{NaCl in } NaAlCl_4)/K_s(\text{NaCl in } KAlCl_4)$ then takes the value of 215 at ~257 °C.

Evaluation of Effective Chloride Concentration Ratios in Various Chloroaluminate Melts. The above K_s ratio is not the only ratio

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Table V. Molar Solubility Constants K_s for the Solubility of an Alkali-Metal Halide MCl in an Alkali-Metal Tetrachloroaluminate Melt M′AlCl$_4$ at 257 °C

MCl	M′AlCl$_4$	K_s = [M$^+$][Cl$^-$], mol^2 L^{-2}	satn concn [M$^+$], mol L^{-1}	satn concn [Cl$^-$], mol L^{-1}
NaCl	KAlCl$_4$	6.78×10^{-3}	0.082	0.082
LiCl	KAlCl$_4$	6.4×10^{-5}	0.008	0.008
NaCl	NaAlCl$_4$	1.46[a]	8.653	0.169
KCl	KAlCl$_4$	3.22[b]	7.985	0.403

[a] An expression for pK_s vs. T in K was given[42] as a function $(A + \Delta C_pT)/(RT) - (B + \Delta C_p(\ln T))/R$, where $A = -11.850$ kJ mol^{-1}, B = -352.81 J mol^{-1} K^{-1}, and $\Delta C_p = 63.26$ J mol^{-1} K^{-1}. [b] An expression for K_s vs. T in K was given[10] as p$K_s = A/T - B$, with $A = 1030$ K and $B = 2.45$.

that is on the order of 100 for the case of sodium tetrachloroaluminate relative to potassium tetrachloroaluminate.

Consider the reaction

$$2\text{AlCl}_4^- \rightleftarrows \text{Cl}^- + \text{Al}_2\text{Cl}_7^- \qquad (7)$$

and the corresponding equilibrium constant, K_1

$$K_1 = \frac{[\text{Cl}^-][\text{Al}_2\text{Cl}_7^-]}{[\text{AlCl}_4^-]^2} \qquad (8)$$

which when expressed in concentrations depends on the temperature, the pressure, and the kind of alkali metal present.

The values of K_1 for NaAlCl$_4$ and KAlCl$_4$ have been determined as a function of temperature by means of the potentiometric method.[10,42] At 257 °C, approximate values of 7.8×10^{-7} and 5.0×10^{-9} can be estimated. We then obtain $K_1^{\text{Na}}/K_1^{\text{K}} = 156$, i.e. a ratio of the same order of magnitude as the one determined from the solubility experiments above.

The reason for the two ratios to be similar in magnitude is believed to be due to the occurrence of stronger M$^+$···Cl$^-$ association in the Na$^+$ case than in the K$^+$ case. This association reduces the *effective* chloride concentration in the NaAlCl$_4$ melt relative to a KAlCl$_4$ melt with the same free chloride formality. In this way, the solubility product, K_s, for NaCl will be higher in NaAlCl$_4$ than in KAlCl$_4$ at saturation. The same argument applies for the case of the K_1's. The *effective* chloride concentration is lower in a melt containing a certain concentration of free chloride with Na$^+$ as the counterion than with K$^+$, and therefore a higher K_1 in the case of Na$^+$ than in the case of K^+ is necessary to obtain equilibrium.

For the case of LiCl saturation in KAlCl$_4$, we find that the solubility product ratio K_s(NaCl in KAlCl$_4$)/K_s(LiCl in KAlCl$_4$) is on the order of 100. Hence, the K_1 equilibrium constants corresponding to eq 7 should take approximately the ratio $K_1^{\text{Li}}/K_1^{\text{Na}} = 100$, if the above argument holds. With the above value of $K_1^{\text{Na}} = 7.8 \times 10^{-7}$, then K_1^{Li} should be approximately 7×10^{-5} or p$K_1^{\text{Li}} = 4.15$ at 257 °C. A pK_1^{Li} value of 4.0 has been determined by Torsi and Mamantov[24] at 250 °C. Data for other pairs of alkali metals are needed to see if this interesting agreement is a coincidence or a more general tendency.

The idea that the difference in solubility of NaCl in NaAlCl$_4$ and in KAlCl$_4$ is mainly due to the association between the cations and the *chloride* ions and to a much lesser extent due to association among the other ions can also be deduced by looking at the equilibrium (eq 9) found in acidic chloroaluminate melts. Øye et al.[43] devised a method to estimate the equilibrium constant for

$$2\text{Al}_2\text{Cl}_7^- \rightleftarrows 2\text{AlCl}_4^- + \text{Al}_2\text{Cl}_6 \qquad (9)$$

this reaction from Raman spectra. A value of 8×10^{-3} for the equilibrium constant corresponding to eq 9, K (expressed in Tempkin mole fractions), was found for the KCl–AlCl$_3$ system in the temperature range 170–240 °C. If the Raman spectra[44] obtained for LiCl–AlCl$_3$, KCl–AlCl$_3$, and CsCl–AlCl$_3$ in the same temperature range as above are compared, it is found that the equilibrium constant K does not vary more than by a factor of 2, depending on the cation. This estimate rests on the reasonable assumption that the scattering factors of the various aluminum chloride species are largely independent of the kind of cation. Our explanation for the relative constancy of K is that since K does not involve the chloride concentration, it can remain quite constant, independent of type of cation. Hence we consider the effect of the interaction between the cations and the chloroaluminate ions to be much smaller than that between the cations and the chloride ions.

If the above given explanation, involving the cation–chloride ion association, is correct, it should apply also to other equilibria in chloroaluminate melts. Unfortunately, as far as we know, no other data is available for which one can compare equilibrium constants obtained in NaAlCl$_4$ and KAlCl$_4$ at the same temperature. For solutions of niobium(V) in tetrachloroaluminate melts in which the equilibrium (eq 10) applies, we were recently able to estimate[45] that the ratio between the equilibrium constants

$$\text{NbCl}_6^- \rightleftarrows \text{NbCl}_5 + \text{Cl}^- \qquad (10)$$

in NaAlCl$_4$ and KAlCl$_4$ is ~100 at 300 °C, in good agreement with the ideas given above. In order to evaluate the general character of such relations, more data are of course indispensable.

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Registry No. KCl, 7447-40-7; AlCl$_3$, 7446-70-0; KAlCl$_4$, 13821-13-1.

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Contribution from the Institute of General Food Chemistry,
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Polarographic Studies on Iron(II) Complexes with Carbamide Derivatives Containing Alkyl Substituents

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Complexation reactions of Fe(II) with carbamide, H$_2$NCONH$_2$ (U), and its aliphatic derivatives such as CH$_3$HNCONH$_2$ (MeU), C$_2$H$_5$HNCONH$_2$ (EtU), CH$_3$HNCONHCH$_3$ (*sym*-Me$_2$U), and C$_2$H$_5$HNCONHC$_2$H$_5$ (*sym*-Et$_2$U) have been studied by the polarographic method. It has been found that, in these systems, there are formed complexes of the type [Fe(H$_2$O)$_{6-n}$X$_n$]$^{2+}$ (n = 1–6). With use of the method of De Ford and Hüme, stability constants β_j and K_j of these complexes were calculated.

Carbamide was well as most of its N-substituted derivatives do not show polarographic activity.[1-3] On the other hand, both carbamide and thiocarbamide reveal a catalytic effect on the behavior of other compounds; e.g. carbamide is used in polaro-

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