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Chloro Complexes in Molten Salts. 9. Potentiometric and Vapor Pressure Study of the System NaCl–AlCl$_3$ in the Temperature Range 175–300 °C

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By means of potentiometric measurements with chlorine/chloride electrode cells, the solubility of NaCl in NaAlCl$_4$ melts was investigated in the temperature range 200–300 °C; the results were combined with previous results at 175 °C. A plot of $-\text{p}K_s$ ($K_s = [\text{Na}^+][\text{Cl}^-]$) vs. the inverse absolute temperature gave a slightly curved relationship in the temperature range 175–300 °C. Based on the assumption of a constant, ΔC°_p, for the solubility reaction, ΔH° could be given as $A + \Delta C^\circ_p T$ and ΔS° as $B + \Delta C^\circ_p \ln T$. The best fit for $-\text{p}K_s$ vs. $1/T$ was obtained for values of ΔC°_p, A, and B of 63.26 J/(mol deg), −11.850 kJ/mol, and −352.81 J/(mol deg), respectively. The uncertainties in ΔH° and ΔS° in the examined temperature range were ca. 3 kJ/mol and ca. 6 J/(mol deg), respectively. In the melts with mole fractions of AlCl$_3$ up to 0.5357$_9$, potentiometric and vapor pressure measurements were best explained by three equilibria: (i) $2\text{AlCl}_4^- \rightleftarrows \text{Al}_2\text{Cl}_7^- + \text{Cl}^-$, (ii) $3\text{Al}_2\text{Cl}_7^- \rightleftarrows 2\text{Al}_3\text{Cl}_{10}^- + \text{Cl}^-$, and (iii) $2\text{Al}_3\text{Cl}_{10}^- \rightleftarrows 3\text{Al}_2\text{Cl}_6 + 2\text{Cl}^-$. The p$K$ values for reaction i were found to be 7.05 (1), 6.74 (1), 6.45 (2), 6.19 (2), 5.94 (3), and 5.70 (4), for reaction ii they are 6.9, 7.2, 7.0, 6.6, 6.3, and 6.1, and for reaction iii there are 14.0, 11.2, 10.7, 10.3, 9.8, and 9.8 at 175, 200, 225, 250, 275, and 300 °C, respectively. For reaction i and on the basis of the assumption of a constant ΔC°_p (different from zero), ΔC°_p, A, and B could be calculated to be 64.00 J/(mol deg), 20.626 kJ/mol, and −415.70 J/(mol deg), respectively, with uncertainties in ΔH° and ΔS° in the examined temperature range of ca. 5 kJ/mol and ca. 10 J/(mol deg), respectively.

Introduction

Chloroaluminate melts have attracted considerable interest because of their special properties as acid/base solvents, for their application in aluminum production, and possibly for their use as electrolytes in rechargeable high-energy-density batteries.

We have previously[2] reported data for the solubility of KCl in KAlCl$_4$ and for the acid/base equilibria in KCl–AlCl$_3$ melts in the temperature range 275–350 °C. Recently[3] the corresponding properties of molten NaCl–AlCl$_3$ were studied potentiometrically, but at one temperature (i.e., 175 °C) only. In the present article, an examination of the temperature dependence of the equilibrium constants for the NaCl–AlCl$_3$ melt system is described.

Several authors[4-8] have investigated the NaCl–AlCl$_3$ system by means of potentiometric and Raman spectroscopic methods. Measurements with aluminum electrodes[4a] (and to a smaller extent chlorine/chloride electrodes[4b]) near the equimolar composition gave evidence for the equilibrium

$$2\text{AlCl}_4^- \rightleftarrows \text{Al}_2\text{Cl}_7^- + \text{Cl}^- \qquad (1)$$

Investigations of melts in a larger compositional range (between ca. 50 and up to ca. 70 mol % AlCl$_3$) have also been performed potentiometrically with aluminum electrodes.[5-7] It was shown in the work by Torsi and Mamantov[5] that eq 1 was in reasonable agreement with the measurements only up to a mole fraction of AlCl$_3$ of ca. 0.55. Boxall et al.[6] explained their measurements in terms of the aluminum species AlCl$_4^-$, Al$_2$Cl$_7^-$, and Al$_2$Cl$_6$ (and AlCl$_3$). Agreement between the measured and calculated values of the potentials at high AlCl$_3$ contents was obtained by varying the activity coefficients of AlCl$_4^-$ according to the theory of a regular solution. Fannin et al.[7] did not take the change in activity coefficients into consideration; on the other hand, they included besides the above mentioned species the existence of Al$_3$Cl$_{10}^-$ on the acidic side in order to obtain better agreement between measured and calculated values. They also compared the equilibrium constant for the equilibrium $\text{AlCl}_4^- + \text{AlCl}_3 \rightleftarrows \text{Al}_2\text{Cl}_7^-$ calculated from the potentiometric measurements (and from the dissociation constant of Al$_2$Cl$_6$) with an equilibrium constant calculated on the basis of the vapor pressure measurements of Narita et al.[9]

Torsi et al.[8] concluded from Raman spectra that the species AlCl$_4^-$, Al$_2$Cl$_7^-$, and Al$_2$Cl$_6$ existed in NaCl–AlCl$_3$ melts (50–73 mol % AlCl$_3$, 225 °C). At compositions with "high AlCl$_3$ contents" a peak appeared which could not be ascribed to any of the above-mentioned species. This was among other things taken as an indication of the presence of a higher polymeric aluminum species, possibly Al$_3$Cl$_{10}^-$. In this connection it should be mentioned that in the related systems KCl–AlCl$_3$ and CsCl–AlCl$_3$ Rytter et al.[10] also found evidence for the formation of AlCl$_4^-$, Al$_2$Cl$_7^-$, and with increasing additions of AlCl$_3$ "higher polymers" (e.g., Al$_3$Cl$_{10}^-$ and Al$_2$Cl$_6$).

Experimental Section

AlCl$_3$ was prepared by reaction of aluminum metal (99.999% from Atomergic Chemetals Corp.) and HCl gas (generated from analytical grade concentrated HCl and concentrated H$_2$SO$_4$). In order to remove surface impurities arising from the machining of aluminum, it was etched in concentrated NaOH solution. After this it was treated in a 12:10:3 v/v/v mixture of 89% H$_3$PO$_4$ and concentrated H$_2$SO$_4$ and HNO$_3$ acids, respectively, in order to smooth the surface and remove traces of oxides. The aluminum was finally washed and dried in nitrogen. The HCl gas was deoxygenated by passing through a column filled with copper (heated to 325 °C) and then dehydrated in three columns filled with P$_2$O$_5$. The reaction between aluminum and HCl was carried out in a quartz tube with a Kanthal heating wire. During the reaction, the temperature was kept just above the melting point of aluminum. The aluminum chloride was condensed in an air-cooled part of the reaction tube and further purified by sublimation under vacuum (residual gas N$_2$) at 170 °C. Anhydrous NaCl was prepared

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from analytical grade material. The purification was achieved by passing HCl through the salt placed in a quartz apparatus, while it was heated to ca. 20 °C above the melting point. The melt was flushed with pure N_2 and was finally filtered and sealed under vacuum.

The experimental techniques concerning the potentiometric and vapor pressure measurements were similar to those used in previous work.[2,11] All weighings and additions to the cells were performed in a nitrogen-filled glovebox with a measured water content of ca. 5 ppm. The chlorine/chloride concentration cell was made of Pyrex, with glassy-carbon rods (V 10 from Carbone Lorraine) as electrode material. The connection tube between the two cell compartments was sealed off after an addition of 0.5 atm of chlorine (Fluka >99.9%) had been made. The furnace used for the potentiometric measurements was the same as described previously.[12] The temperature was measured by chromel–alumel thermocouples (from Pyrotenax) calibrated at the freezing points of pure tin and lead to within ±0.5 °C.

General Considerations

The formality C' is defined as the initial molar amount of one of the salts (i.e., NaCl or $AlCl_3$) dissolved in 1 L of the melt. The excess formality of NaCl or $AlCl_3$, C'(excess) is defined as the difference in formality between NaCl and $AlCl_3$ or $AlCl_3$ and NaCl, respectively. Melts containing more than 50 mol % $AlCl_3$ are called acidic, and melts with more than 50 mol % NaCl are the basic melts. The pCl is defined as the negative logarithm of the chloride ion concentration (in molar units). The densities necessary for calculations of molar and formal concentrations were obtained from the work of Boston.[13]

The electrochemical cell used for the potentiometric measurements was of the type: glassy carbon, $Cl_2|Cl_I^-(NaCl\text{–}AlCl_3)|$ceramic pin$|Cl_{II}^-(NaCl_{sat}\text{–}AlCl_3)|Cl_2$, glassy carbon. I and II refer to the measurement and reference compartments, respectively. A melt saturated with NaCl at the appropriate temperature was used for reference purposes. It has previously been shown[2] that the cell voltage (ΔE) of similar type concentration cells measuring the chloride activity in KCl–$AlCl_3$ melts is within the experimental uncertainty given by eq 2 in

$$\Delta E = (-RT/F) \ln ([Cl^-]_{II}/[Cl^-]_I) \qquad (2)$$

the compositional range 47 to 52 mol % KCl. In this case the higher limit of ca. 52 mol % KCl is due to the rather low solubility of KCl in $KAlCl_4$ in the examined temperature range. The lower limit of ca. 47 mol % was obtained on the basis of estimations over variations in activity coefficients and estimations of errors due to neglecting some of the terms in the general equation for the potential. By analogy it is assumed that eq 2 is valid also for the NaCl–$AlCl_3$ system in the smaller concentration range 48–50.6 mol % NaCl investigated in the present work. The higher limit (of 50.6 mol % NaCl) is here due to the low solubility of NaCl in $NaAlCl_4$ at the measured temperatures. The pCl of the melt can then be expressed as eq 3 where pCl_{II} is the pCl in the melt saturated with NaCl.

$$pCl_I = -(F/(RT \ln 10))\Delta E + pCl_{II} \qquad (3)$$

In the basic region (except close to the 1:1 composition), the only aluminum complex present is $AlCl_4^-$.[3-8] Therefore, addition of NaCl gives rise to a corresponding amount of chloride ions. Accordingly the pCl of such melts will be equal to −log C'(NaCl, excess). Thus a plot of $(-F/(RT \ln 10))\Delta E$ against −log C'(NaCl, excess) should give a straight line with a slope of unity and an intercept at the abscissa ($\Delta E = 0$) corresponding to pCl_{II} at the temperature in question.

Results and Discussion

Table I. Values of Mole Fraction (X) and Cell Potentials for Molten NaCl–$AlCl_3$ in the Temperature Range 200–300 °C[a]

	$-\Delta E$, mV				
X_{NaCl}	200 °C	225 °C	250 °C	275 °C	300 °C
0.4802_0	349.1	350.9	352.6		
0.4834_3				343.9	346.4
0.4837_9	340.5	342.2	343.6		
0.4866_4				332.6	333.8
0.4869_2	331.0	331.5	332.7		
0.4898_1				319.3	320.0
0.4903_1	318.3	318.5	318.1		
0.4931_4				300.3	299.9
0.4935_7	300.1	299.1	298.8		
0.4937_7	299.1	298.2	297.5		
0.4967_3				265.6	265.0
0.4969_7	269.2	266.6	264.3		
0.5016_3	19.1_0				
0.5016_7	20.1_4	33.5_0			
0.5020_1	11.1_8	23.7_9	36.9_6		
0.5021_5	11.3_4	24.3_7			
0.5024_1	3.9_8	15.9_2			55.9_2
0.5024_9	4.3_1				
0.5025_0	2.8_0	15.3_3			
0.5026_1	3.2_0				
0.5027_9		9.4_4	22.2_0	35.6_3	49.0_1
0.5031_6		4.3_4	16.6_2	29.7_9	42.8_7
0.5038_3			8.2_3	20.4_6	33.5_4
0.5049_4				8.5_8	21.1_5
0.5056_7					14.1_5

[a] Values obtained at 175 °C have been given previously.[3]

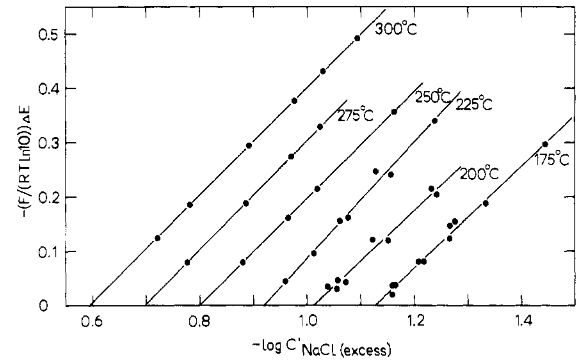

Figure 1. Plots used to check eq 3 for the NaCl–$AlCl_3$ system in the temperature range 175–300 °C. The values at 175 °C are from previous work.[3]

Determination of the Solubility of NaCl in $NaAlCl_4$. From eq 3 it is evident that it is necessary to know the compositions of the saturated melts, used in the reference electrode compartment, in order to determine the pCl values of a given melt. In Table I all measured values of mole fractions and cell potentials are given. The measurements with mole fractions of NaCl greater than 0.500 used to calculate the values of $-(F(RT \ln 10))\Delta E$ and −log C' (NaCl, excess) are listed in Table II and plotted in Figure 1. The straight lines in this figure are drawn by use of a least-squares method. The weighted average of the slopes is found to be 0.99 (4). The theoretical value of 1.00 lies within the limits of the uncertainty. Therefore, in Table III, the pCl values and the compositions of the saturated melts have been calculated for the individual temperatures with fixed slopes of unity. It can be seen from Table III that the variance for each of the measured temperatures vary considerably. There is no obvious way to explain this discrepancy. In Table III is also given the molar concentrations of sodium and chloride ions in the saturated melts. The product of $[Na^+]$ and $[Cl^-]$ in these melts is equal to K_s (the solubility product constant) (i.e., eq 4). The logarithm of this constant plotted as a function of the inverse absolute temperature is shown in Figure 2. The plot is slightly

$$[Na^+][Cl^-] = K_s \qquad (4)$$

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Table II. Values Used To Obtain the Solubility of NaCl in $NaAlCl_4$ in the Temperature Range 175-300 °C

175 °C[a]		200 °C		225 °C		250 °C		275 °C		300 °C	
−log C'(NaCl, excess)	$-F\Delta E/(RT \ln 10)$	−log C'(NaCl, excess)	$-F\Delta E/(RT \ln 10)$	−log C'(NaCl, excess)	$-F\Delta E/(RT \ln 10)$	−log C'(NaCl, excess)	$-F\Delta E/(RT \ln 10)$	−log C'(NaCl, excess)	$-F\Delta E/(RT \ln 10)$	−log C'(NaCl, excess)	$-F\Delta E/(RT \ln 10)$
1.1601	0.0366	1.0379	0.0341	0.9592	0.0439	0.8803	0.0793	0.7756	0.0789	0.7204	0.1244
1.1613	0.0197	1.0559	0.0298	1.0128	0.0955	0.9647	0.1601	0.8859	0.1881	0.7812	0.1860
1.1641	0.0373	1.0574	0.0459	1.0613	0.1551	1.0183	0.2139	0.9702	0.2739	0.8915	0.2949
1.2083	0.0795	1.0720	0.0424	1.0774	0.1611	1.1624	0.3561	1.0238	0.3276	0.9759	0.3770
1.2177	0.0805	1.1223	0.1208	1.1279	0.2466					1.0295	0.4310
1.2662	0.1225	1.1515	0.1191	1.1569	0.2407					1.0941	0.4917
1.2664	0.1464	1.2321	0.2145	1.2375	0.3389						
1.2758	0.1540	1.2417	0.2035								
1.3337	0.1876										
1.4448	0.2963										

[a] Values calculated from previous work.[3]

Table III. Composition of Saturated Melts in the Temperature Range 175-300 °C

temp, °C	pCl	X_{NaCl}[a]	var[d] × 10^8	$[Na^+]$, M	$[Cl^-]$, M
175[b]	1.128 (6)	0.502 09 (5)[c]	0.20	8.936	0.0745
200	1.020 (5)	0.502 72 (4)	0.53	8.843	0.0955
225	0.907 (5)	0.503 56 (4)	0.56	8.756	0.124
250	0.804 (1)	0.504 57 (1)	0.05	8.674	0.157
275	0.6967 (4)	0.505 91 (1)	0.004	8.599	0.201
300	0.598 (1)	0.507 51 (2)	0.05	8.531	0.252

[a] Other component $AlCl_3$. [b] Values at 175 °C calculated from previous work.[3] [c] I.e., 0.502 09 ± 0.000 05. [d] var = variance.

curved, indicating variance of $\Delta H°$ and $\Delta S°$ in the rather large temperature range investigated. Further the increase in heat capacity as a consequence of the reaction, $\Delta C°_p$, must be different from 0. There is no a priori reason why it should be 0, and the simplest way of modeling the thermodynamics for the NaCl dissolution is to consider $\Delta C°_p$ as temperature independent. In this case the values of $\Delta H°$ and $\Delta S°$ can be given as $A + \Delta C°_p T$ and $B + \Delta C°_p \ln T$, respectively, where A and B are constants. From the data points in Table II (or the values in Table III) and with equal weights for all points $\Delta C°_p$, A and B are found to be 63.26 J/(mol deg), −11.850 kJ/mol, and −352.81 J/(mol deg), respectively. The many significant figures are necessary in order to obtain a good fit between measured and calculated pK_s values (standard error in estimate 0.0022). However, the standard errors in $\Delta C°_p$ and A are 5.8 J/(mol deg) and 2.9 kJ/mol, respectively. $\Delta H°$ and $\Delta S°$ can be calculated from the given constants to be 25 (3) kJ/mol and 50 (6) J/mol deg) at 312.5 °C (the uncertainty in $\Delta S°$ is estimated from the uncertainty in $\Delta H°$). These values are of the same order of magnitude as for the dissolution of KCl in $KAlCl_4$ where $\Delta H°$ and $\Delta S°$ were found to be 19.7 (6) kJ/mol and 46.8 (11) J/(mol deg), respectively.[2] In this latter case invariance of $\Delta H°$ and $\Delta S°$ with temperature was assumed in the rather small examined temperature range 275–350 °C (i.e., average temperature 312.5 °C).

The obtained values for the dissolution of NaCl in $NaAlCl_4$ can also be used to calculate the composition of the melt at the eutectic temperature 150 °C found by Fisher and Simon.[14] Their value for the mole fraction of NaCl at this temperature was 0.50_0 which is in good agreement with a value of 0.501 60 (1) found by use of the above given thermodynamic equations. Further data to compare with are the solubility data of Torsi and Mamantov[5] from which pCl of the saturated melts can be calculated to be 0.80_4 and 0.61_9 at 250 and 300 °C, respectively. These values should be compared with the values of 0.804 (1) and 0.598 (1) listed in Table III for the same temperatures. The pCl of the saturated melt at 175 °C has

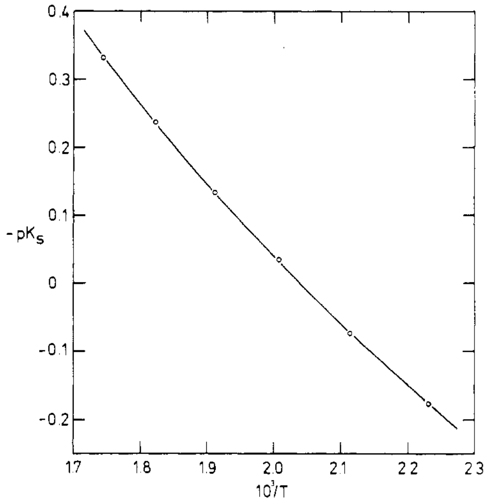

Figure 2. −pK_s (K_s is the solubility product for Na^+ and Cl^- ions) as a function of the inverse absolute temperature (×10^3).

previously[3] been compared with literature values.

Model Equilibria for the NaCl–AlCl$_3$ System Based on Potentiometric Measurements. Three different models are in the present investigation (as in the analogous KCl–$AlCl_3$ system[2]) examined in order to explain the measured cell potentials for the acidic NaCl–$AlCl_3$ system:

model 1

$$\begin{gathered} 2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^- \\ Al_2Cl_7^- \rightleftarrows Al_2Cl_6(\text{soln}) + Cl^- \\ \text{equilibrium constants } K_1 \text{ and } K_2 \end{gathered} \tag{5}$$

model 2

$$\begin{gathered} 2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^- \\ 3Al_2Cl_7^- \rightleftarrows 2Al_3Cl_{10}^- + Cl^- \\ \text{equilibrium constants } K_1 \text{ and } K_3 \end{gathered} \tag{6}$$

model 3

$$\begin{gathered} 2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^- \\ 3Al_2Cl_7^- \rightleftarrows 2Al_3Cl_{10}^- + Cl^- \\ 2Al_3Cl_{10}^- \rightleftarrows 3Al_2Cl_6(\text{soln}) + 2Cl^- \\ \text{equilibrium constants } K_1,\ K_3, \text{ and } K_4 \end{gathered} \tag{7}$$

In Table IV the calculated equilibrium constants for models 1–3 are shown. These constants are obtained by varying the equilibrium constants for each model systematically so that the least deviation between measured and calculated results (for measurements with X_{NaCl} (i.e., mole fractions) lower than 0.500) is obtained. Due to the limited situation examined in

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Table IV. Comparison between Three Different Models for the NaCl-$AlCl_3$ System at Different Temperatures

equilibria	model no.	p*K*, var × 10^8					
		175 °C[a]	200 °C	225 °C	250 °C	275 °C	300 °C
$2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$	1	7.046 (3)	6.739 (3)	6.450 (5)	6.190 (5)	5.938 (6)	5.695 (12)
$Al_2Cl_7^- \rightleftarrows Al_2Cl_6 + Cl^-$		6.10 (3), 0.36	5.84 (3), 0.34	5.58 (5), 1.01	5.32 (5), 1.00	5.01 (6), 0.59	4.88 (13), 2.34
$2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$	2	7.053 (3)	6.745 (5)	6.455 (7)	6.195 (7)	5.944 (5)	5.700 (12)
$3Al_2Cl_7^- \rightleftarrows 2Al_3Cl_{10}^- + Cl^-$		6.8 (1), 0.33	6.6 (2), 0.58	6.3 (2), 1.23	6.1 (3), 1.29	5.7 (2), 0.37	5.6 (5), 1.95
$2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$	3	7.05 (1)	6.74 (1)	6.45 (2)	6.19 (2)	5.94 (3)	5.70 (4)
$3Al_2Cl_7^- \rightleftarrows 2Al_3Cl_{10}^- + Cl^-$		6.9[b]	7.2[b]	7.0[b]	6.6[b]	6.3[b]	6.1[b]
$2Al_3Cl_{10}^- \rightleftarrows 3Al_2Cl_6 + 2Cl^-$		14.0,[b] 0.36	11.2,[b] 0.55	10.7,[b] 1.38	10.3,[b] 1.42	9.8,[b] 0.75	9.8,[b] 3.15

[a] Values from previous work.[3] [b] Large uncertainties in calculated standard errors (see text).

Table V. Values of Mole Fraction (*X*) and Vapor Pressure of Molten NaCl-$AlCl_3$ in the Temperature Range 250-300 °C

X_{AlCl_3}	vapor pressure, mmHg								
	250 °C			275 °C			300 °C		
		calcd			calcd			calcd	
	measd[a]	model 1	model 3	measd[a]	model 1	model 3	measd[a]	model 1	model 3
0.5102_0	2	4	2	3	7	3	4	8	3
0.5159_2	4	9	4	5	16	7	7	19	7
0.5260_2	8	25	12	11	41	19	19	51	19
0.5357_9	15	46	22	27	76	35	40	96	37

[a] With the pressure due to dissolved gases, mainly N_2, subtracted.

model 3 (very small concentrations of both $Al_3Cl_{10}^-$ and Al_2Cl_6), the calculated standard errors in pK_3 and pK_4 become (unrealistic) large in the computer program calculations.[15] In this connection it is interesting to note the falling tendency of both pK_3 and pK_4 with increasing temperature, indicating that the results in these extreme situations probably still have a physical meaning. This point of view is further supported by a calculation[15] of the 95% nonlinear confidence limits which seem to give more realistic uncertainties. (For pK_3 and pK_4, the limits were as follows: at 175 °C, 6.88-6.93, 14.0-15.1; at 200 °C, 7.2-7.4, 11.2-11.6; at 225 °C, 6.9-7.2, 10.7-11.5; at 250 °C, 6.6-6.9, 10.3-10.9; at 275 °C, 6.3-6.8, 9.8-11.2; at 300 °C, 6.1-7.2, 9.7-∞.) The variances (based on mole fractions) for all three models are not significantly different. It can also be seen that these variances are somewhat higher than (the average of) the variances for the solubility data (Table III). The two sets of variances may, however, not be comparable since they are obtained under rather different circumstances. The conclusion is that it is not possible from the potentiometric measurements alone to distinguish between the different models.

The pK_1 values at a given temperature are almost the same for all three models. These values agree (where they can be compared) reasonable well with those found by Torsi annd Mamantov[5] and by Boxall et al.[6] In Figure 3 is shown a plot of pK_1 (model 3) vs. the inverse absolute temperature. This plot is slightly curved for the same reason as that mentioned in connection with the temperature dependence of the solubility product of NaCl in $NaAlCl_4$. On the basis of the assumption that $\Delta C°_p$ is different from 0 (and constant), $\Delta C°_p$, *A*, and *B* were found to be 64.00 J/(mol deg), 20.626 kJ/mol, and −415.70 J/(mol deg), respectively. The standard errors in $\Delta C°_p$ and *A* were 9.5 J/(mol deg) and 4.8 kJ/mol, respectively. This means that at 265 °C the values of $\Delta H°$ and $\Delta S°$ are 55 (5) kJ/mol and −13 (10) J/(mol deg), respectively. These values are in reasonable agreement with the results of Boxall et al.,[6] who for the temperature range 175-355 °C (average value 265 °C) found 52.49 (2) kJ/mol and −17.2 (12) J/(mol deg), respectively. By comparison, the corresponding values for the KCl-$AlCl_3$ melts[2] in the temperature range 275-350 °C (average value 312.5 °C) were found to be 86.0 (12) kJ/mol and 0.9 (22) J/(mol deg), respectively. These latter values should be compared with the values 58 (5) kJ/mol and −8 (10) J/(mol deg) calculated for the present system at 312.5 °C.

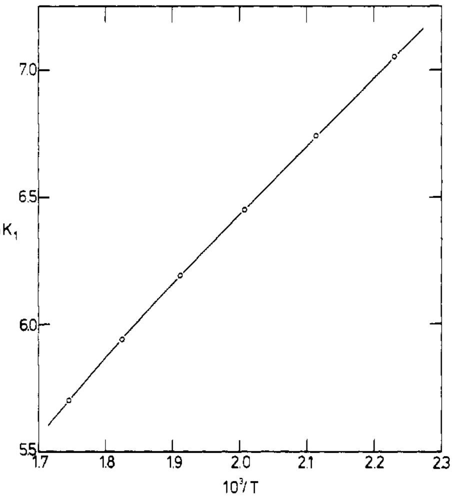

Figure 3. pK_1 values (from model 3, Table IV) as a function of the inverse absolute temperature (×10^3).

Vapor Pressure Measurements and Model Equilibria for the NaCl-$AlCl_3$ System. A possibility for obtaining information about the proposed models for the equilibria in NaCl-$AlCl_3$ melts is to include vapor pressure measurements in the considerations. In Table V the vapor pressures over molten NaCl-$AlCl_3$ are given in the temperature range 250-300 °C. The values in this table have been corrected for dissolved gases by extrapolation of the logarithm of the measured pressure vs. the mole fraction of $AlCl_3$ down to $X_{AlCl_3} = 0.5000$; under these conditions, vapor pressure over the melts is neglegible (i.e., when the special degassing procedure for basic melts described earlier[2] was used on the equimolar NaCl-$AlCl_3$ system, a vapor pressure of less than 0.2 mmHg was obtained at 300 °C). In this way, the pressures due to dissolved gases were found by extrapolation to be 3, 3, and 4 mmHg at 250, 275, and 300 °C, respectively. Unfortunately, no other vapor pressure measurements have been performed in the concen-

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(15) Based on a program NLIN by D. W. Marquardt. See also: Marquardt, D. W. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431.

tration range from 50 to ca. 53 mol % $AlCl_3$ in which it can be assumed that the variations in activity coefficients are neglegible. At a composition almost identical with our $AlCl_3$ richest composition (i.e., at 53.6 mol % $AlCl_3$), vapor pressures of 27, 42, and 61 mmHg at 250, 275, and 300 °C, respectively, can be obtained from the diagram of Dewing.[16] These values are somewhat higher than our values but agree however well with the vapor pressures of Viola et al.[17] (at temperatures where the values can be compared).

It is obvious that model 2 can be neglected since it involves no uncharged species and could therefore only give rise to insignificant vapor pressures. Calculations using the pK values for models 1 and 3 from the potentiometric measurements and based on the assumption that the vapor pressure over the melt is propertional to the species fraction of Al_2Cl_6 in the melt (Raoult's law) are also shown in Table V. The vapor pressures of liquid Al_2Cl_6 necessary to make these calculations are from the work of Smits and Meijering.[18] As discussed in connection with the vapor pressure measurements of KCl–$AlCl_3$ melts[2] there is no a priori reason to expect Raoult's law to be correct at low Al_2Cl_6 concentrations in the MCl–$AlCl_3$ systems (M = Li, Na, K, Rb, Cs), even though for the KCl–$AlCl_3$ system[2] it was found that calculations based on Raoult's law and Henry's law seemed to agree reasonably well. In the present case involving small vapor pressures, the measurements were not accurate enough to use Henry's law. It was, however, found that the pressures calculated from Raoult's law with model 1 were 2–3 times higher than the measured vapor pressures, whereas the calculated vapor pressures with model 3 are much closer to the measured values.

It is clear that the uncertainties in the calculated vapor pressures for model 3 must be rather high. An idea of these uncertainties can be obtained by using the 95% nonlinear confidence ranges found for pK_4 (at 250 °C the calculated vapor pressure ranges are approximately from the measured vapor pressures to 50% above the measured vapor pressures, at 275 °C the ranges are approximately from 50% below to 30% above the measured vapor pressures, and at 300 °C the ranges are from 0 and up to the measured vapor pressures). However, the rather good agreement between the measured and calculated vapor pressures for model 3 at three different temperatures indicates that this may have a physical meaning (despite the uncertainties in these values and the use of Raoult's law) and that model 3 therefore gives the most realistic description of the reactions in acidic NaCl–$AlCl_3$ melts. This is as previously mentioned also in agreement with Raman spectra on MCl–$AlCl_3$ melts[8,10] and with the results obtained on the KCl–$AlCl_3$ system.[2] Further potentiometric and vapor pressure measurements, especially at higher temperatures (and consequently at higher vapor pressures), but also on other MCl–$AlCl_3$ systems, should hopefully give information to prove or disprove the above ideas.

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Studies of Phosphazenes. 12.[1] Reactions of $N_4P_4Cl_8$ with Dibenzylamine. Isolation of an Unusual "Bicyclic" Phosphazene, $N_4P_4[N(CH_2Ph)_2]_6(NCH_2Ph)$

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Octachlorocyclotetraphosphazene, $N_4P_4Cl_8$, reacts with dibenzylamine to give the chloro(dibenzylamino) derivatives, $N_4P_4Cl_{8-n}[N(CH_2Ph)_2]_n$, $n = 1$, 2 (two isomers), and 4 (three isomers). Nongeminal structures have been assigned to these compounds on the basis of ^1H and ^{31}P NMR spectra. The presence of at least two tris(dibenzylamino) derivatives in some reaction mixtures is also inferred from NMR spectra. Steric effects become important at the tetrakis stage of chlorine replacement, and further substitution by dibenzylamine to give monocyclic tetrameric derivatives does not occur. A "bicyclic" phosphazene, $N_4P_4[N(CH_2Ph)_2]_6(NCH_2Ph)$, is obtained from the reaction of $N_4P_4Cl_8$ with an excess of dibenzylamine in boiling methyl cyanide. The formation of this derivative and its spectroscopic data are discussed.

Introduction

Although numerous reactions of chlorocyclophosphazenes with amines have been investigated,[4] the importance of steric effects in influencing the chlorine replacement pattern has not been evaluated in any detail. Reactions of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, with the bulky reagents dibenzylamine,[5] dicyclohexylamine,[6] and *P,P,P*-triphenylmonophosphazene, $HN{=}PPh_3$,[7] terminate at the bis stage of chlorine replacement, an observation that has been attributed mainly to steric factors. It is of interest to study the reaction of a sterically demanding nucleophile with the more reactive homologue[4,8] octachlorocyclotetraphosphazene, $N_4P_4Cl_8$ (I). In this paper, the results of a systematic investigation of the reaction between $N_4P_4Cl_8$ (I) and dibenzylamine are reported. In addition to several chloro(dibenzylamino)cyclotetraphosphazenes, an unusual "bicyclic" phosphazene is formed.[9] The distinctive spectroscopic features of the latter are highlighted.

Results and Discussions

Chloro(dibenzylamino)cyclotetraphosphazenes and the Chlorine Replacement Pattern. The chloro(dibenzylamino) derivatives, $N_4P_4Cl_{8-n}[N(CH_2Ph)_2]_n$ (II–VII), isolated from the reaction of dibenzylamine with the octachloride (I) possess nongeminal disposition of the dibenzylamino substituents (Figure 1). The structural assignments for these compounds

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