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Supplementary Material Available: Tables S1 and S2, reporting observed and calculated structure factor amplitudes and thermal parameters for non-hydrogen atoms (8 pages). Ordering information is given on any current masthead page.

Contribution from Chemistry Department A,
The Technical University of Denmark, DK-2800 Lyngby, Denmark

Chloro Complexes in Molten Salts. 10. Potentiometric and Spectrophotometric Study of the System KCl–AlCl$_3$–CuCl$_2$ at 300 °C

J. H. von BARNER,* P. B. BREKKE, and N. J. BJERRUM*

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The formation of complexes of Cu(II) in KCl–AlCl$_3$ melts at 300 °C (in some cases saturated with CuCl$_2$) has been studied by potentiometric and spectrophotometric measurements. With the Cu(II) concentration in the range 0.10–1 M and with the pCl range 0.38–6.0 the results could be explained by the following equilibria: (i) $CuCl_4^{2-} \rightleftarrows CuCl_3^- + Cl^-$; (ii) $CuCl_3^- \rightleftarrows CuCl_2 + Cl^-$; (iii) $CuCl_2 \rightleftarrows CuCl^+ + Cl^-$; (iv) $CuCl_2(soln) \rightleftarrows CuCl_2(s)$. p*K* values (based on molar concentrations) for reactions i–iii: for 0.10 M Cu(II), 1.14 (4), 3.17 (26), 5.4 (3); for 0.31 M Cu(II), 0.99 (2), 3.29 (2), no value found; for 1 M Cu(II), 0.79 (4), 3.55 (3), no value found. By comparison, the p*K* for reaction i calculated from spectrophotometric measurements on 0.10 M solutions of Cu(II) in KCl–AlCl$_3$ melts at 300 °C was in the range −0.1 to +1.9. The maximum obtainable molar concentration of CuCl$_2$ (determined by reaction iv) was from the potentiometric measurements calculated to be 0.005 (3). This is in good agreement with a value of 0.0031 (8) obtained from the spectrophotometric measurements. Finally, the spectra of $CuCl_4^{2-}$, $CuCl_3^-$, and CuCl$_2$ were calculated from measured spectra of KCl–AlCl$_3$–CuCl$_2$ melts.

Introduction

The Cu(II) complexes formed in the KCl–AlCl$_3$–CuCl$_2$ system were examined as part of a general examination of solute species in chloroaluminate melts. However, it is also interesting to note that related systems such as KCl–CuCl$_2$/CuCl–LaCl$_3$ and KCl–CuCl/CuCl$_2$[1–3] melts have industrial applications due to their catalytic properties.

Not much work has been performed concerning the identity of the formed Cu(II) species in the related alkali chloride melts,[4–7] and almost nothing seems to be known of the species in alkali chloride–aluminum chloride melts; however, an examination of CuCl$_2$ in liquid aluminum chloride has been reported.[8]

In melts with very high chloride activity such as molten CsCl,[6] the presence of the tetrahedral coordinate copper(II) was based on comparison with solid Cs$_2$CuCl$_4$ and Cs$_2$ZnCl$_4$ (doped with Cu^{2+}), which both have known crystal structures. Also in the LiCl–KCl eutectic melt the observed spectra of Cu(II) were believed to be due to tetrahedral coordinate copper(II), though somewhat distorted.[5]

Due to the rather few experiments made on chloride melts, it is useful to compare these results with experiments made in other nonaqueous solvents such as acetonitrile,[9,10] anhydrous acetic acid,[11] dimethylformamide,[12] propylene carbonate,[13] and dimethyl sulfoxide.[13] The main results of these measurements seem to indicate formation in the dilute systems of the mononuclear complexes CuCl$^+$, CuCl$_2$, $CuCl_3^-$, and $CuCl_4^{2-}$. The complexes are in some cases strongly solvated in some cases probably very weakly solvated.

In connection with an examination of acidic chloroaluminate melts, it is also interesting to make comparison with recent results on complex formation in the gaseous phase between CuCl$_2$ and aluminum chloride. Raman and visible–ultraviolet spectra have shown that copper(II) chloride forms gas-phase complexes such as CuAl$_2$Cl$_8$ and CuAlCl$_5$.[14–16] The most likely structure of the first compound is a distorted-octahedral structure (with $AlCl_4^-$ as a tridentate ligand) or a square-planar structure (with $AlCl_4^-$ as a bidentate ligand[17]). The structure of the second compound can be visualized as a tetracoordinated copper atom with one chloride and one tridentate $AlCl_4^-$ ligand.

Experimental Section

The chemicals used for the solvent were prepared in the same way as in recent work dealing with KCl–AlCl$_3$ melts.[18] The CuCl$_2$ used was obtained by a method described and evaluated previously.[19]

In some of the experiments where it was necessary to add very small amounts of copper to the melt, a special procedure was applied. The phase diagram for aluminum–copper[20] shows that with a copper content smaller than 5.65 wt % completely miscibility in the solid phase is obtained at 548 °C. The solubility of copper in aluminum decreases rapidly as the temperature decreases; however, in alloys with less than 4–5 wt % copper it is easy to keep the copper homogeneously dissolved in the aluminum by rapid cooling to room temperature. An alloy containing 98.49 wt % aluminum (99.999% pure) and 1.51 wt % Cu (99.99% pure)

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(1) Ruthven, D. M.; Kenney, C. N. *Chem. Eng. Sci.* **1967**, *22*, 1561.
(2) Ruthven, D. M.; Kenney, C. N. *Chem. Eng. Sci.* **1968**, *23*, 981.
(3) (a) Riegel, H.; Schindler, H. D.; Sze, M. C. *Chem. Eng. Prog.* **1973**, *69*, 89. (b) *AIChE Symp. Ser.* **1973**, *69* (No. 135), 96.
(4) Harrington, G.; Sundheim, B. R. *Ann. N.Y. Acad. Sci.* **1960**, *79*, 950.
(5) Gruen, D. M.; McBeth, R. L. *Pure Appl. Chem.* **1963**, *6*, 23.
(6) Smith, G. P.; Griffith, T. R. *J. Am. Chem. Soc.* **1963**, *85*, 4051.
(7) Wilmshurst, J. K. *J. Chem. Phys.* **1963**, *39*, 1779.
(8) Øye, H. A.; Gruen, D. M. *Inorg. Chem.* **1964**, *3*, 836.
(9) Manahan, S. E.; Iwamoto, R. T. *Inorg. Chem.* **1965**, *4*, 1409.
(10) Baaz, M.; Gutmann, V.; Hampel, G.; Masaguer, J. R. *Monatsh. Chem.* **1962**, *93*, 1416.
(11) Sawada, K.; Ohtaki, H.; Tanaka, M. *J. Inorg. Nucl. Chem.* **1972**, *34*, 3455.
(12) Elleb, M.; Meullemeestre, J.; Schwing-Weil, M. J.; Vierling, F. *Inorg. Chem.* **1980**, *19*, 2699.
(13) Elleb, M.; Meullemeestre, J.; Schwing-Weil, M. .; Vierling, F. *Inorg. Chem.* **1982**, *21*, 1477.
(14) Emmenegger, F. P.; Rohrbasser, C.; Schläpfer, C. W. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 127.
(15) Schläpfer, C. W.; Rohrbasser, C. *Inorg. Chem.* **1978**, *17*, 1623.
(16) Papatheodorou, G. N.; Capote, M. A. *J. Chem. Phys.* **1978**, *69*, 2067.
(17) Brooker, M. H.; Papatheodorou, G. N. In "Advances in Molten Salt Chemistry"; Mamantov, G., Ed.; Elsevier: Amsterdam, Oxford, New York, Tokyo, 1983; Vol. 5.
(18) von Barner, J. H.; Bjerrum, N. J.; Smith, G. P. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 837.
(19) Andreasen, H. A.; Mahan, A.; Bjerrum, N. J. *J. Chem. Eng. Data* **1981**, *26*, 195.
(20) Kirk-Othmer "Encyclopedia of Chemical Technology", 2nd ed.; Wiley Interscience: New York, London, 1963; Vol. 1, p 958.

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was prepared under a cover of argon (<0.1 ppm O_2). As an extra precaution (against formation of nitride) the resulting alloy was weighed after the mixing had taken place. (It was found that the weight of the alloy was within 0.01 mg identical with the weight of the used metals.)

All handling of the solid salts was performed in a nitrogen-filled glovebox with continuous gas purification by forced recirculation through external molecular sieves.

The electrochemical cells were made of Pyrex with glassy-carbon-rod electrodes (Carbone-Lorraine) fused into the bottom. The cells were filled with chlorine (Fluka >99.9%) at various pressures. One problem encountered in the present work was that at high acidity (i.e., at high pCl values) Cu(II) tended to be reduced to Cu(I). In order to diminish this tendency, pressures of up to 8 atm chlorine were used. Pressures of more than 1 atm were achieved by freezing the chlorine with liquid N_2 before sealing the cell. The type of furnace used for the potentiometric measurements has been described previously.[21]

The optical cells were of fused quartz. Short path length (less than 0.1 mm) was obtained by placing precision-ground fused-silica inserts into 5-mm cells. The spectra were measured with a Cary 14R spectrophotometer equipped with a system for punching out spectral data on paper tape.

As in the case of the potentiometric measurements at high pCl values (i.e. higher than 5.5), it was necessary to keep a pressure of more than 1 atm above the melt. In one case especially this was a serious problem because of the absorption due to the chlorine band around 32×10^3 cm^{-1}. In this case in order to obtain the highest reproducibility it was necessary to add the copper chloride enclosed in a small easily breakable ampule. The absorption due only to the added $CuCl_2$ could then be obtained as the difference between a spectrum measured before and after the ampule was broken (and $CuCl_2$ dissolved). With this procedure, no change in chlorine pressure occurs since the pressures in the ampule and the cell were equal (0.5 atm at room temperature).

The temperatures in the present work were measured by chromel–alumel thermocouples calibrated to within ±0.5 °C at the freezing points of pure tin, lead, and zinc.

General Considerations

The initial molar amount of one of the added substances (in the present work KCl, $AlCl_3$, $CuCl_2$, or Cu (in Al–Cu alloy)) dissolved in 1 L of melt is defined as its formality, C'. The pCl is defined as the negative logarithm of the chloride ion concentration (in molar units). The formal absorptivity is defined by A/lC', where A is the absorbance (corrected for the absorbance of the cell and solvent) and l is the path length. The compositions of the melts are given either in mole fractions such as X_{KCl}, X_{AlCl_3}, or X_{CuCl_2} or in the notation KCl/$AlCl_3$/$CuCl_2$. The KCl/$AlCl_3$/$CuCl_2$ notation is used to indicate the molar ratios of KCl, $AlCl_3$, and $CuCl_2$ that were weighed. This is so because in some melts precipitations occur that affect the relative amounts of the weighed substances. The densities necessary for calculation of molar and formal concentration were obtained from the work of Morrey and Carter[22] and Andreasen et al.[23]

The electrochemical cell used for the potentiometric measurements was of the type glassy carbon,Cl_2|Cl^-_I(KCl–$AlCl_3$–$CuCl_2$)|ceramic pin|Cl^-_{II}(KCl_{sat}–$AlCl_3$)|Cl_2,glassy carbon. I and II refer to the measurement and reference compartments, respectively. It has previously been shown[24] 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 1 in the compositional range of 47–52 mol

$$\Delta E = (-RT/F) \ln ([Cl^-]_{II}/[Cl^-]_I) \qquad (1)$$

% KCl (or 53–48 mol % $AlCl_3$). In this case, the higher limit of ca. 52 mol % KCl was due to the rather low solubility of KCl in $KAlCl_4$ at 300 °C. 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. In the present case the concentration of Cu(II) in some of the experiments is increased in order to examine the deviations obtained by exceeding these limits (i.e., 47–52 mol % for KCl or 53–48 mol % for $AlCl_3$). However, also in the case where a high concentration of Cu(II) is present, the system is treated as for the more ideal systems assuming eq 1 to be correct. This means that the pCl of the melt is expressed by eq 2 where pCl_{II} is the pCl of the melt saturated

$$pCl_I = -(F/(RT \ln 10))\Delta E + pCl_{II} \qquad (2)$$

with KCl. The average experimental coordination number $\bar{n}$ is defined in the normal way[24-26] complexes in solution. In the present case where we are dealing with solute species with a limited solubility, it is, however, important to define a number that can be used when a precipitate is present and in this way utilize a larger compositional range. Such a number can be expressed by $\bar{n}'$, which is defined in eq 3, where $n_{CuCl_2,w}$ is the number of moles of $CuCl_2$

$$\bar{n}' = (C'_{KCl} + 3C'_{AlCl_3} + 2n_{CuCl_2,w}/V - [Cl^-] - 4[AlCl_4^-] - 7[Al_2Cl_7^-] - 10[Al_3Cl_{10}^-] - 6[Al_2Cl_6])V/n_{CuCl_2,w} \qquad (3)$$

that were weighed (but not necessarily the number of moles in solution) and V is the volume of the melt. The difference between $\bar{n}'$ and $\bar{n}$ is therefore in the present case only a matter whether one considers the moles of $CuCl_2$ that were weighed or the actual number of moles of $CuCl_2$ in solution. The concentrations of $AlCl_4^-$, $Al_2Cl_7^-$, and $Al_3Cl_{10}^-$ were calculated on the basis of the pK values obtained for the self-dissociation of the KCl–$AlCl_3$ solvent at 300 °C[27] (i.e., (i) $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$, (ii) $3Al_2Cl_7^- \rightleftarrows 2Al_3Cl_{10}^- + Cl^-$, and (iii) $2Al_3Cl_{10}^- \rightleftarrows 3Al_2Cl_6(soln) + 2Cl^-$, with p$K$ values 7.80, 7.3, and 14.5, respectively).

The evaluation of the importance of various possible complexes of Cu(II) formed is (as in previous work[28]) based on a general model expressed by eq 4–6, where v_i, x_i, y_i, and z_i are all integers. From the model put forward to explain the changes in the melt (for example, eq 4 and 5) and from arbitrarily chosen equilibrium

$$v_1CuCl_4^{2-} \rightleftarrows Cu_{v_1}Cl_{z_1}{}^{2v_1-z_1} + (4v_1 - z_1)Cl^- \qquad (4)$$

$$v_2Cu_{v_1}Cl_{z_1}{}^{2v_1-z_1} \rightleftarrows x_2Cu_{y_2}Cl_{z_2}{}^{2y_2-z_2} + (z_1v_2 - x_2z_2)Cl^- \qquad (5)$$

$$v_iCu_{y_{i-1}}Cl_{z_{i-1}}{}^{2y_{i-1}-z_{i-1}} \rightleftarrows x_iCu_{y_i}Cl_{z_i}{}^{2y_i-z_i} + (z_{i-1}v_i - x_iz_i)Cl^- \qquad (6)$$

constants, the concentration of each species can be calculated. These values can be used to calculate an $\bar{n}$ value that can be compared with the experimentally determined value of $\bar{n}$. The best values of the equilibrium constants (i.e., giving the minimum deviations between measured and calculated values) can be found by a computer program that furthermore calculates the minimum variance for each model. The ratio between the so-obtained minimum variances for different models and the model giving the lowest minimum variance (since experimental variances could not be obtained in the present case) is then compared. On the basis of an F-test, the distinction was made between models with a probability of more or less than 90%. In the tables each model with probability higher than 90% is marked with an asterisk.

The spectra obtained were treated by a linear least-squares method developed especially for our spectral work.[29-31] Similar methods are known from the literature.[32,33] The method used

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(21) Andreasen, H. A.; Bjerrum, N. J.; Foverskov, C. E. *Rev. Sci. Instrum.* **1977**, *48*, 1340.

(22) Morrey, J. R.; Carter, D. G. *J. Chem. Eng. Data* **1968**, *13*, 94.

(23) Andreasen, H. A.; Mahan, A.; Bjerrum, N. J. *J. Chem. Eng. Data* **1981**, *26*, 195.

(24) von Barner, J. H.; Bjerrum, N. J. *Inorg. Chem.* **1973**, *12*, 1891.

(25) Bjerrum, N. *Kgl. Danske Vidensk. Selsk. Skr., Nat.-Mat. Afd.* **1915**, *12* (4).

(26) Bjerrum, J. "Metal Ammine Formation in Aqueous Solution"; P. Haase and Son: Copenhagen, 1941, reprinted 1957.

(27) Brekke, P. B.; von Barner, J. H.; Bjerrum, N. J. *Inorg. Chem.* **1979**, *18*, 1372.

(28) Andreasen, H. A.; Bjerrum, N. J. *Inorg. Chem.* **1978**, *17*, 3605.

(29) Fehrmann, R.; Bjerrum, N. J.; Andreasen, H. A. *Inorg. Chem.* **1975**, *14*, 2259.

(30) Fehrmann, R.; Bjerrum, N. J.; Poulsen, F. W. *Inorg. Chem.* **1978**, *17*, 1195.

(31) Fehrmann, R.; Bjerrum, N. J.; Pedersen, E. *Inorg. Chem.* **1982**, *21*, 1497.

(32) Lieto, L. R. Thesis, 1969; Report ORNL-TM-2714; Oak Ridge National Laboratory: Oak Ridge, TN, 1969.

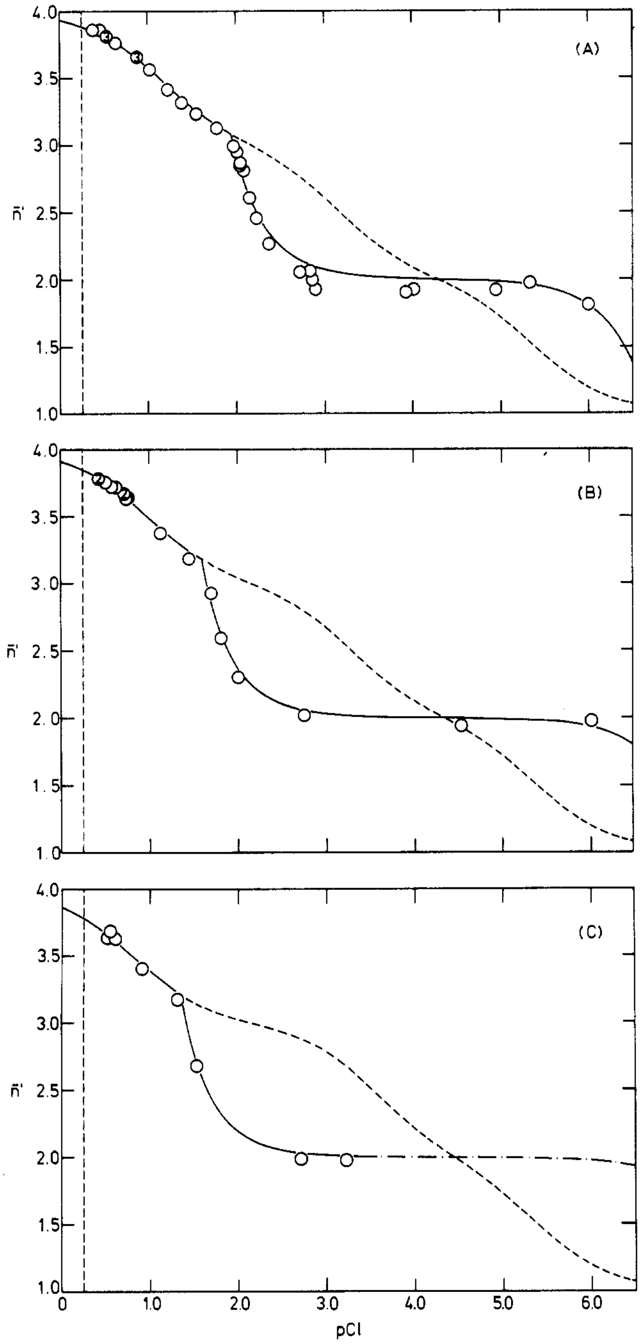

Figure 1. Average experimental coordination number (with precipitate included) ($\bar{n}'$) for Cu(II) in KCl–AlCl$_3$ at 300 °C as a function of pCl. The formal concentration of CuCl$_2$ (at the pCl ranges where no precipitate was present) were as follows: A, 0.10 M CuCl$_2$; B, 0.31 M CuCl$_2$; C, 1 M CuCl$_2$. Calculated values of $\bar{n}$ are indicated by full curves. The dashed curves show as hypothetical extrapolations what would happen if no precipitation occurred. The vertical dashed lines show the limiting pCl, due to saturation with KCl.

Table I. Values of Weighed Molar Ratios and Cell Potentials for KCl–AlCl$_3$–CuCl$_2$ at 300 °C and with 0.10 M CuCl$_2$ in Melts without Precipitate

$-\Delta E$, mV	weighed molar ratios KCl/AlCl$_3$/CuCl$_2$		
13.6_8	0.5165_1	0.4769_0	0.0066_0
23.1_8	0.5141_4	0.4792_3	0.0066_3
30.9_8	0.5122_9	0.4812_3	0.0064_8
30.9_8	0.5122_9	0.4812_2	0.0064_9
31.3_4	0.5122_1	0.4813_1	0.0064_7
43.1_7	0.5100_5	0.4834_3	0.0065_2
69.8_4	0.5065_8	0.4868_7	0.0065_5
70.5_6	0.5065_2	0.4869_3	0.0065_5
70.8_1	0.5064_5	0.4869_9	0.0065_6
87.4_5	0.5049_4	0.4884_8	0.0065_8
110.2	0.5033_1	0.4901_4	0.0065_5
128.9	0.5023_7	0.4911_0	0.0065_4
147.2	0.5016_9	0.4917_6	0.0065_5
173.8	0.5009_5	0.4924_9	0.0065_5
196.0	0.5003_2	0.4931_2	0.0065_6
199.7	0.5001_7	0.4932_7	0.0065_5
203.8	0.4998_9	0.4932_7	$0.0068_4{}^a$
204.3	0.4998_4	0.4933_6	$0.0068_0{}^a$
208.4	0.4997_6	0.4947_7	$0.0054_7{}^a$
216.4	0.4988_8	0.4942_9	$0.0068_3{}^a$
225.0	0.4983_5	0.4948_7	$0.0067_8{}^a$
240.9	0.4976_5	0.4956_0	$0.0067_5{}^a$
280.5	0.4968_5	0.4963_9	$0.0067_6{}^a$
293.1	0.4969_4	0.4964_8	$0.0065_8{}^a$
296.5	0.4966_5	0.4966_1	$0.0067_4{}^a$
300.1	0.4964_1	0.4968_8	$0.0067_1{}^a$
417.8	0.4960_8	0.4972_0	$0.0067_2{}^a$
427.9	0.4960_8	0.4972_0	$0.0067_2{}^a$
533.3	0.4937_4	0.4996_0	$0.0066_6{}^a$
577.5	0.4900_4	0.5033_5	$0.0066_1{}^a$
653.4	0.4659_2	0.5272_4	$0.0068_4{}^{a,b}$

[a] Visible precipitate present in melt. [b] Chlorine pressure above melt ca. 8.2 atm (in contrast to the normally used pressure of ca. 1 atm).

Table II. Values of Weighed Molar Ratios and Cell Potentials for KCl–AlCl$_3$–CuCl$_2$ at 300 °C and with 0.31 M CuCl$_2$ in Melts without Precipitate

$-\Delta E$, mV	weighed molar ratios KCl/AlCl$_3$/CuCl$_2$		
20.1_1	0.5195_7	0.4606_5	0.0197_8
21.7_0	0.5191_6	0.4610_5	0.0197_9
29.3_3	0.5173_0	0.4628_6	0.0198_4
37.6_2	0.5154_7	0.4647_1	0.0198_2
43.3_0	0.5145_3	0.4656_5	0.0198_2
53.8_5	0.5125_7	0.4676_0	0.0198_3
54.5_3	0.5125_8	0.4675_5	0.0198_7
58.3_5	0.5118_8	0.4682_5	0.0198_7
56.7_4	0.5119_6	0.4681_9	0.0198_6
100.5	0.5060_8	0.4739_8	0.0199_5
137.2	0.5029_6	0.4769_6	0.0200_7
165.8	0.4998_9	0.4800_6	$0.0200_6{}^a$
178.5	0.4964_1	0.4836_0	$0.0200_0{}^a$
200.7	0.4932_8	0.4866_0	$0.0201_2{}^a$
285.6	0.4901_1	0.4896_5	$0.0202_5{}^a$
488.1	0.4882_0	0.4914_4	0.203_7

[a] Visible precipitate present in melt.

is based on the Bouguer–Beer law and the law of additive absorbances expressed as a general equation involving three matrices (eq 7), where l_m is the path length at the mth composition, C_{mi}

$$[l_mC_{mi}][\epsilon_i(\nu_n')] = [A_m(\nu_n')] \qquad (7)$$

is the concentration of the ith species for the mth composition, $\epsilon_i(\nu_n')$ is the molar absorptivity of the ith species at the wavenumber ν_n', and $A_m(\nu_n')$ is the total absorbance of the mth composition at the wavenumber ν_n'.

This equation can be solved for a set of equilibrium constants associated with a given model (eq 4–6), and the corresponding spectra of the individual species can be plotted. The computer program can, by changing the equilibrium constants systematically, lead to the equilibrium constants that give the minimum deviation (i.e., least squares) between the measured and calculated spectra.

Results and Discussion

Potentiometric Measurements. One of the problems in the present investigation, and many other investigations dealing with solutions of metal chlorides in chloroaluminate melts, is the low solubility encountered for these salts at pCl values around the point of neutrality. As described in General Considerations a new number $\bar{n}'$ (instead of $\bar{n}$) was defined so that it was possible to extract some more useful information from these saturated so-

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(33) Björck, Å. *BIT* **1967**, *7*, 1,257.

Table III. Values of Weighed Molar Ratios and Cell Potentials for $KCl-AlCl_3-CuCl_2$ at 300 °C and with 1 M[a] $CuCl_2$ in Melts without Precipitate

$-\Delta E$, mV	weighed molar ratios $KCl/AlCl_3/CuCl_2$		
29.8_0	0.5288_6	0.4097_2	0.0614_3
33.7_3	0.5302_1	0.4069_2	0.0628_6
39.9_1	0.5275_3	0.4092_5	0.0632_2
74.4_5	0.5164_6	0.4211_6	0.0623_9
120.0	0.5074_6	0.4243_8	0.0681_6
144.8	0.4900_3	0.4414_7	0.0685_0[b]
279.2	0.4673_4	0.4680_1	0.0646_5[b]
337.1	0.4669_5	0.4684_5	0.0646_0[b]

[a] The concentration of Cu(II) varied between 0.99 and 1.08 M (average 1.02 (4) M). [b] Visible precipitate present in melt.

lutions. In Tables I–III are given the measured potentials for a series of concentration cells with either completely dissolved or partly dissolved $CuCl_2$. In Figure 1 is given three plots of the $\bar{n}'$ values (at three different concentrations) vs. the pCl of the solution. The full curves in Figure 1 are calculated on the basis of the self-dissociation reaction for the solvent (described in General Consideration) and a stepwise dissolution of $CuCl_4^{2-}$ to $CuCl^+$, i.e. the reactions

$$CuCl_4^{2-} \rightleftarrows CuCl_3^- + Cl^- \quad (8)$$

$$CuCl_3^- \rightleftarrows CuCl_2 + Cl^- \quad (9)$$

$$CuCl_2 \rightleftarrows CuCl^+ + Cl^- \quad (10)$$

$$CuCl_2(soln) \rightleftarrows CuCl_2(s) \quad (11)$$

with equilibrium constants K_1, K_2, and K_3 for the first three equilibria (i.e., (8)–(10)), respectively. It will later be shown that these are in fact (except for eq 10 where not enough experiments are available) the equilibria giving the best agreement between the measured and calculated values. The dashed curves show by hypothetical extrapolations what the curves would look like if no precipitation occurred and the equilibrium constants for the reactions remained the same. The vertical dashed lines show the limiting pCl, due to saturation with KCl. It should be noted (as already mentioned in General Considerations) that the limits in the compositional range for the solvent of 47–52 mol % KCl (or 53–48 mol % $AlCl_3$) are exceeded for the solution containing 1 M $CuCl_2$, and care should be taken in the evaluation of the results obtained at this concentration.

In order to examine whether the reactions given in eq 8 and 9 really give the best description of the system, an examination of the general equations (4)–(6) was persuaded. The results of such an examination is shown in Tables IV and V. This examination was of course limited to the basic part of the system where no precipitation occurred. The concentration ranges examined are as already mentioned rather small, which seriously limits the usefulness of this procedure, especially at higher Cu(II) concentrations (whereas it is difficult at low concentrations to obtain high enough accuracy to make a valuable examination). In the present case the examination has been limited to the 0.10 and 0.31 M solutions. Models with higher than 90% probability (compared with the lowest minimum variances) are marked with asterisks in Tables IV and V. From Table IV it is clear that the significantly preferable model for the first step in the dissociation of $CuCl_4^{2-}$ is formation of $CuCl_3^-$ (i.e., eq 8), whereas there are more possibilities for the next step. The lowest variance is, however, obtained for formation of $CuCl_2$ (i.e., eq 9). For the 0.31 M solution (Table V) the picture is almost the same, with $CuCl_3^-$ as the best choice for the first dissociation product. As in the case of 0.10 M $CuCl_2$ there are more possibilities for the next step; however, the formation of $CuCl_2$ gives a very low variance. From these results it seems safe to conclude (not taking solutions with very high concentrations of Cu(II) in consideration) that the next significantly stable species after $CuCl_4^{2-}$ with rise of pCl is $CuCl_3^-$ (i.e., eq 8). The next step is probably represented by eq 9, but this is not certain. However, by including the measurements on the saturated systems it is possible to say something more definite about the reliability of eq 9. Since we know from X-ray powder diagrams that the precipitate consists of solid $CuCl_2$, a solubility reaction must involve $CuCl_2$ (as given in eq 11) or a polymer of $CuCl_2$ such as Cu_2Cl_4 or Cu_3Cl_6. The calculated solubilities for such species are given in Table VI. It can be seen that the solubility calculated by using the model involving $CuCl_2$ is much lower than for the model involving Cu_2Cl_4 or Cu_3Cl_6. A comparison with the solubility determined by a spectrophotometric

Table IV. Minimum Variances (×10⁴)[a] Based on Potentiometric Measurements for Models[b] for 0.10 M $CuCl_2$ in $KCl-AlCl_3$ at 300 °C

	$Cu_{v_1}Cl_{z_1}^{2v_1-z_1}$							
$Cu_{y_2}Cl_{z_2}^{2y_2-z_2}$	$Cu_2Cl_7^{3-}$	$CuCl_3^-$	$Cu_2Cl_6^{2-}$	$Cu_2Cl_5^-$	$CuCl_2$	Cu_2Cl_4	$CuCl^+$	Cu^{2+}
no complex	*c*	31.94	30.35	624.8	959.3	1393.3	1519.7	1736.7
$CuCl_3^-$	34.23							
$Cu_2Cl_6^{2-}$	23.0	21.73						
$Cu_2Cl_5^-$	104.4	2.49*[d]	25.07					
$CuCl_2$	112.2	2.09*	24.55	1451.2				
Cu_2Cl_4	228.3	3.10*	20.19	671.0	1272.6			
$CuCl^+$	226.4	3.06*	20.11	740.6	2132.0	2851.6		
Cu^{2+}	285.3	4.14*	18.49	699.2	1540.5	2087.2	1628.4	

[a] Number of measurements, 16. [b] Given generally by $v_1CuCl_4^{2-} \rightleftarrows Cu_{v_1}Cl_{z_1}^{2v_1-z_1} + (4v_1 - z_1)Cl^-$ and $v_2Cu_{v_1}Cl_{z_1}^{2v_1-z_1} \rightleftarrows x_2Cu_{y_2}Cl_{z_2}^{2y_2-z_2} + (z_1v_2 - x_2z_2)Cl^-$. [c] There is no reason to make a calculation here, since $\bar{n}$ cannot be lower than 3.5 for this model. [d] Asterisks are based on $F_{0.10}(14.14) = 2.03$ (for two-equilibria models) and $F_{0.10}(15.14) = 2.01$ (for one-equilibrium models).

Table V. Minimum Variances (×10⁴)[a] Based on Potentiometric Measurements for Models[b] for 0.31 M $CuCl_2$ in $KCl-AlCl_3$ at 300 °C

	$Cu_{v_1}Cl_{z_1}^{2v_1-z_1}$							
$Cu_{y_2}Cl_{z_2}^{2y_2-z_2}$	$Cu_2Cl_7^{3-}$	$CuCl_3^-$	$Cu_2Cl_6^{2-}$	$Cu_2Cl_5^-$	$CuCl_2$	Cu_2Cl_4	$CuCl^+$	Cu^{2+}
no complex	*c*	7.88	14.43	462.3	628.8	1040.6	1037.5	1142.8
$CuCl_3^-$	8.72							
$Cu_2Cl_6^{2-}$	5.06	4.35*[d]						
$Cu_2Cl_5^-$	20.49	1.88*	16.10					
$CuCl_2$	17.49	1.97*	16.50	593.7				
Cu_2Cl_4	50.26	2.58*	16.05	514.8	700.8			
$CuCl^+$	45.31	2.52*	16.06	593.8	700.3	3076.3		
Cu^{2+}	61.86	3.03*	16.04	540.5	1104.2	2055.4	1161.5	

[a] Number of measurements, 11. [b] Given generally by $v_1CuCl_4^{2-} \rightleftarrows Cu_{v_1}Cl_{z_1}^{2v_1-z_1} + (4v_1 - z_1)Cl^-$ and $v_2Cu_{v_1}Cl_{z_1}^{2v_1-z_1} \rightleftarrows x_2Cu_{y_2}Cl_{z_2}^{2y_2-z_2} + (z_1v_2 - x_2z_2)Cl^-$. [c] There is no reason to make a calculation here, since $\bar{n}$ cannot be lower than 3.5 for this model. [d] Asterisks are based on $F_{0.10}(9.9) = 2.44$ (for two-equilibria models) and $F_{0.10}(10.9) = 2.42$ (for one-equilibrium models).

Table VI. Solubilities (mol/L) Calculated from Potentiometric Measurements[a] for Different Possible Models[b]

$\nu_2 = 1$	$\nu_2 = 2$	$\nu_2 = 3$
0.005 (3)	0.014 (3)	0.017 (6)

[a] Total concentration of Cu(II) in the ranges where no precipitate is present is 0.10 mol/L. [b] $Cu_{\nu_2}Cl_{2\nu_2}$.

Table VII. p*K* Values for Cu(II) Equilibria in $KAlCl_4$ Based on Cell Potentials

equilibria	0.10 M $CuCl_2$[a]	0.31 M $CuCl_2$[a]	1 M[b] $CuCl_2$[a]
$CuCl_4^{2-} \rightleftarrows CuCl_3^- + Cl^-$	1.14 (4)	0.99 (2)	0.79 (4)
$CuCl_3^- \rightleftarrows CuCl_2 + Cl^-$	3.17 (26)	3.29 (2)	3.55 (3)
$CuCl_2 \rightleftarrows CuCl^+ + Cl^-$	5.38 (30)	*c*	*c*

[a] The concentration is only valid for the pCl ranges where no precipitate is present. [b] The concentration of Cu(II) varied between 0.99 and 1.08 M (average 1.02 (4) M). [c] No value could be calculated here to the lack of data, instead the value 5.38 found for a 0.10 M solution of $CuCl_2$ was used in order to obtain the values for pK_1 and pK_2.

method (to be described later) shows that the value obtained by assuming $CuCl_2$(soln) as the formula for the dissolved copper chloride gives a value very close to the one obtained by the spectrophotometric method (namely 0.0031 (8) mol/L). Therefore, eq 9 must be considered a significantly better model than the one involving Cu_2Cl_4(soln) or Cu_3Cl_6(soln) (even if the uncertainty in the values is taken into consideration).

The curves shown in Figure 1 are calculated by including eq 10 in the calculations. At present we are not able to verify the existence of this equilibrium. On the other hand, it is clear that the precipitated $CuCl_2$ dissolves as the melt is made more acidic, indicating the formation of a new copper species. Since the copper species in the more basic melts are all mononuclear, the best guess is that this species is also mononuclear and is given by eq 10. Further, this is consistent with observations for other media.[9-11] In Table VII are shown the best values for the equilibrium constants for eq 8–10 at the three different examined concentrations. It can be seen that no value has been calculated for pK_3 for the two highest Cu(II) concentrations. In order to make the hypothetical plots shown in Figure 1 the pK_3 value and the value for the solubility of $CuCl_3$ used are the ones obtained for 0.10 M Cu(II).

The observed variation for each of the p*K* values (pK_1, pK_2, pK_3) as the total concentration is increased must be due both to changes in the activity coefficients as well as to changes that are not accounted for in the expression for the measured potentials (i.e., eq 1). Interesting is the steady increase in the p*K* values observed as the number of ligands decreases. It can also be seen that the difference between pK_1 and pK_2 for 0.10 M $CuCl_2$ is 2.03 and the difference between pK_2 and pK_3 is 2.2. That these differences are approximately equal is rather interesting because an examination of the results obtained for the $KCl-AlCl_3-TeCl_4$ system[34] also gives approximately equal differences, and furthermore such behavior is typical of p*K* values of chloro complexes in aqueous solutions.[35]

As already mentioned, in the very acidic part of the $KCl-AlCl_3$ system the measured potentials are dependent on the chlorine pressure above the melt. In one case (i.e., the last measurement in Table I) a pressure as high as 8.2 atm (at 300 °C) was applied to make sure that no decomposition of Cu(II) to Cu(I) took place. By varying the pressure above this melt, it was found that rather little change in the measured potentials was observed, after a pressure of 1.7 atm had been reached (i.e., from 1.7 to 8.2 atm, a change of 1.5 mV) whereas there was a considerable change below 1.7 atm (i.e., a change of more than 30 mV from 1.7 to 0.2 atm).

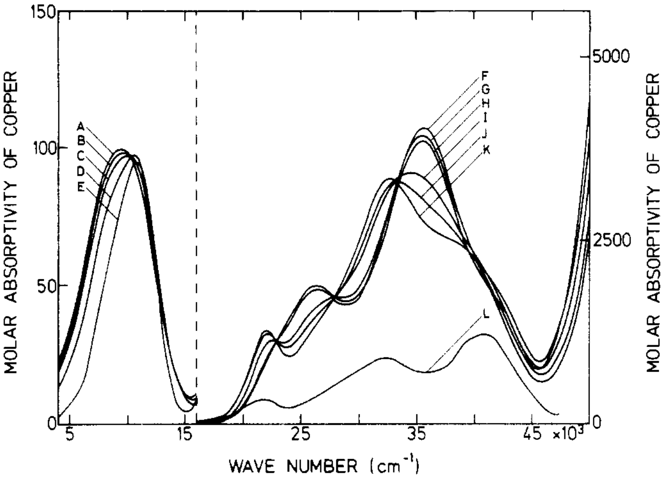

Figure 2. Series of spectra of Cu(II) in $KCl-AlCl_3$ melts at 300 °C. The mole fractions of KCl, $AlCl_3$, and formal concentrations of $CuCl_2$ as well as $\bar{n}$ and pCl values are given in Table VIII.

Table VIII. Values of Composition, Formal Concentration of $CuCl_2$, $\bar{n}$, and pCl for $KCl-AlCl_3-CuCl_2$ Melts[a] at 300 °C

	mole fraction			calcd values[b]	
spectrum	KCl	$AlCl_3$	C'_{CuCl_2}, mol/L	$\bar{n}$	pCl
A	0.5087_1	0.4874_1	0.0591_7	3.75_2	0.65_4
B	0.5080_6	0.4855_2	0.0982_6	3.70_7	0.75_2
C	0.5061_9	0.4874_1	0.0977_5	3.63_0	0.89_6
D	0.5032_3	0.4904_0	0.0969_5	3.45_0	1.24_5
E	0.4998_3	0.4999_5	0.0033_4	2.29_2	3.52_9
F	0.5183_0	0.4751_3	0.1013	3.86_7	0.32_2
G	0.5133_8	0.4799_8	0.1019	3.81_8	0.48_5
H	0.5172_4	0.4763_1	0.0992	3.86_0	0.35_1
I	0.5056_6	0.4875_9	0.1031	3.60_0	0.95_6
J	0.5033_0	0.4900_7	0.1010	3.43_1	1.24_3
K	0.5018_1	0.4915_4	0.1011	3.26_2	1.54_2
L	0.4991_9	0.5004_2	0.0058_3	1.99_4	4.29_2

[a] From which the spectra in Figure 2 have been obtained. [b] Calculated on the basis of p*K* values for eq 8–10 of 1.14, 3.17, and 5.4, respectively, and the self-dissociation constants for the solvents given in the text.

Spectrophotometric Measurements. We have found that the average coordination number for chloride decreases as the melt is made more acidic. Similarly it is observed that the spectra of the solution change as the acidity/basicity of the melt changes. Such spectral changes are shown in Figure 2. Values of composition, formal concentration of $CuCl_2$, $\bar{n}$, and pCl for the melts that have given rise to the spectra shown in Figure 2 are given in Table VIII. Because of the great difference in molar absorptivity between the near-infrared bands and the bands in the visible–ultraviolet part of the spectrum it was necessary to work with cells with different path lengths for the two ranges and also with somewhat different compositions for the two ranges.

It is clear from Figure 2 that there is one isosbestic point in the near-infrared (spectra A–D) region and three reasonably well-defined isosbestic points in the visible–ultraviolet (spectra F–K) region. Further, it is clear that as the chloride activity decreases, the bands at 26.2 × 10^3 and 35.5 × 10^3 cm^{-1} and the shoulder at 41 × 10^3 cm^{-1} decrease and some new bands at 21.8 × 10^3, 32.1 × 10^3, and 39.1 × 10^3 cm^{-1} increase. Such behavior is exactly what one would expect for a change predominantly from $CuCl_4^{2-}$ to $CuCl_3^-$.

Furthermore, the spectra can be treated by the linear least-squares method discussed in General Considerations. On the basis of the p*K* values obtained from the potentiometric measurements (0.10 M solutions of $CuCl_2$), it is possible to calculate the spectra of pure $CuCl_4^{2-}$ and $CuCl_3^-$. These spectra are given in Figure 2. It is, however, also possible to calculate the value of the equilibrium constant K_1 from these measurements. By using the visible range (650–350 nm with steps of 1 nm), a p*K* region (95% confidence) of −0.14 to +1.86 could be calculated. This compares

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(34) von Barner, J. H.; Bjerrum, N. J.; Kiens, K. *Inorg. Chem.* **1974**, *13*, 1708.

(35) Rossotti, F. J. "Modern Coordination Chemistry"; Lewis, J., Wilkins, R. G., Eds.; Interscience: New York, 1960; pp 1–77.

Table IX. Absorption Maxima for Chloro Complexes of Cu(II) in KCl–AlCl$_3$ at 300 °C and in Other Media [ν_{max}, 10^3 cm^{-1} (ϵ_{max}, M^{-1} cm^{-1})]

	dimethylformamide[12]	dimethyl sulfoxide[13]	propylene carbonate[13]	KCl–AlCl$_3$ (300 °C)	Al$_2$Cl$_6$ gas (172 °C)[16]
$CuCl_4^{2-}$	8.3 (120)	8.3 (124)	8.3 (113)	8.8 (108)	
	24.3 (2080)	24.4 (2710)	24.4 (2650)	26.2 (1980)	
	33.8 (4700)	33.9 (5840)	33.9 (5710)	35.6 (4220)	
			41.5 (2240)	41.8[a] (1840)	
$CuCl_3^-$	9.1 (97)	9.5 (103)	9.3 (69)		
			11.2 (86)	11.0 (104)	
	22.7 (820)	22.7 (650)	21.3 (1670)	21.8 (1550)	
	26.3 (1000)[a]	26.3 (1300)[a,b]			
	33.3 (3520)	33.6 (3760)	31.7 (3750)	32.0 (3770)	
			39.7 (2690)	39.0 (2340)	
$CuCl_2$			11.5 (76)	11.0 (95)	
				18.7 (70)	
			21.3 (730)		
				26.1 (250)	
			31.7 (2100)		
				36.1 (560)	
			38.3 (3360)		
				41.2 (650)	
$CuCl_2 \cdot Al_2Cl_6$					11.7 (80)
					30.5 (3030)[b]
					38.0 (1520)[a,b]
					47.5 (1310)[b]

[a] Shoulder. [b] Taken from graph.

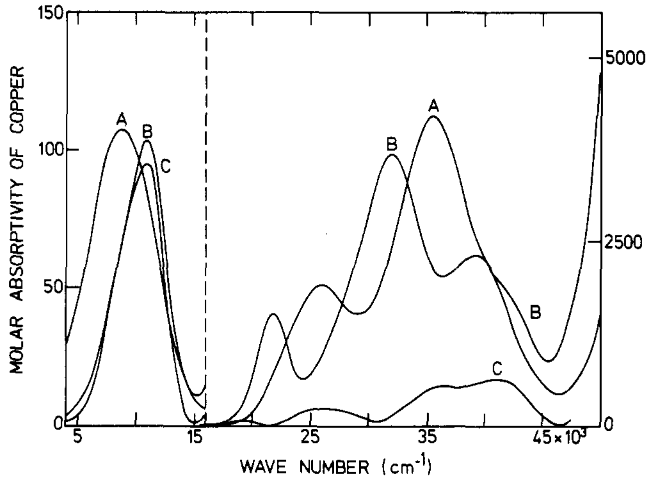

Figure 3. Calculated spectra: A, $CuCl_4^{2-}$; B, $CuCl_3^-$; C, $CuCl_2$.

very well with the value of 1.14 (4) found by the potentiometric method. By using data from the near-infrared part of the spectrum in the calculations (i.e., the range from 2600 to 600 nm in steps of 6 nm), a pK region of −0.13 to +1.44 is found. This is in good agreement with the result obtained from the visible range.

The conclusion must be that the spectrophotometric measurements yield results that compare well with those obtained from the potentiometric measurements and furthermore that it is possible to obtain the spectra of $CuCl_4^{2-}$ and $CuCl_3^-$. These spectra are shown in Figure 3.

The spectrum of $CuCl_2$ is a little complicated to obtain because the solubility of $CuCl_2$ is very low in the pCl range where $CuCl_2$ is the predominant species. Consequently, it is necessary to work with very small concentrations. It is also necessary to work with high chlorine pressures at high pCl values in order to avoid formation of Cu(I). This is not a problem in the near-infrared range of the spectrum (spectrum E in Figure 2). However, because of the presence of chlorine, the absorption in part of the visible and ultraviolet range is high and not so well-defined due to the way the chlorine is added. The method described in the Experimental Section was therefore used in order to avoid a change in the chlorine pressure by addition of $CuCl_2$. Since from the potentiometric measurements we know the values of equilibrium constants for the equilibria between $CuCl_4^{2-}$, $CuCl_3^-$, $CuCl_2$, and Cl^-, we are able by means of our computer program to calculate the spectrum of $CuCl_2$. The resulting spectrum of $CuCl_2$ in the near-infrared and visible range is shown in Figure 3. Finally, something should be said about the spectrophotometric determination of the solubility of $CuCl_2$. In order to determine this solubility the absorbance at 21.3×10^3 cm^{-1} was measured for a series of solutions that contained increasing amounts of $CuCl_2$ over a pCl range where the predominant species is $CuCl_2$. As mentioned in the Experimental Section, in this range we are dealing with very dilute solutions. It was therefore necessary to add the copper in the form of an Al–Cu alloy. The result of this examination is graphically shown in Figure 4. At the given pCl (5.0–5.2) it can be seen from Figure 1 that the average experimental coordination number is below 2 (on average 16% below). The total solubility determined from Figure 4 (0.0047 (1) mol/L) should therefore be reduced by amounts corresponding to [$CuCl^+$] and [$CuCl_3^-$] in solution. Such a procedure gives a value of 0.0031 (8) mol/L for the solubility of $CuCl_2$ at 300 °C. This is of course under the assumption that the species formed is $CuCl^+$.

Comparison with the Spectra of Chloro Complexes Obtained in Other Media. A comparison with the spectra of chloro complexes in other nonaqueous media is interesting especially as regards solvation. It has been assumed but not always expressed clearly that there is likely to be less solvation in chloroaluminate melts than in other solvents. Examples with less solvation (lower coordination number than that expected)[36] and with normal solvation (with the expected coordination number) have been found.[37]

Some recent and accurate measurements on the complexes of Cu(II) in dimethylformamide,[12] dimethyl sulfoxide,[13] and propylene carbonate[13] are interesting for comparison purposes. The spectra of the individual chloro complexes were obtained in much the same way as in the present case. Comparison between these and our own spectra is made in Table IX. A spectrum of $CuAl_2Cl_8$ in the gas phase[16] is also included.

If we look at the spectra due to $CuCl_4^{2-}$, it can be seen that there is a reasonable similarity between the band positions in the three other solvents and in KCl–AlCl$_3$. This is to be expected since it is to be assumed that $CuCl_4^{2-}$ is not solvated since Cu(II) has obtained its preferred coordination number. It can furthermore be seen that there is a greater similarity between the band positions obtained in the three other nonaqueous solvents than between these and the band positions in the molten salt solvent. This difference may be explained by the difference in temperature. It should be noted that the lowest molar absorptivity is found for the molten

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(36) Brynestad, J.; Smith, G. P. *J. Am. Chem. Soc.* **1970**, *92*, 3198.
(37) Andreasen, H. A.; Bjerrum, N. J. *Inorg. Chem.* **1978**, *17*, 3605.

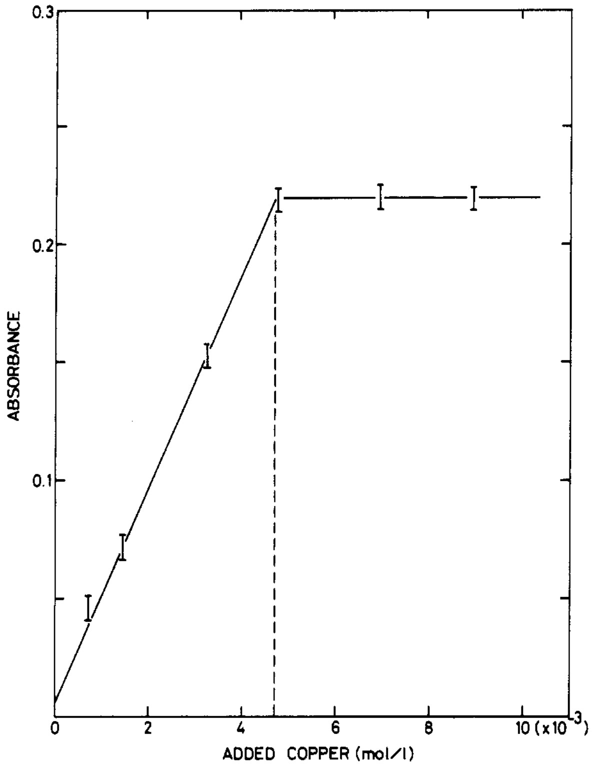

Figure 4. Solubility of Cu(II) in acidic KCl–AlCl$_3$ melts at 300 °C determined spectrophotometrically at 21.3 × 10^3 cm^{-1}. The pCl and $\bar{n}$ ranges were 5.5–5.2 and 1.60–1.72, respectively.

salt systems; this is in agreement with the observation that an increase in temperature broadens the bands and lowers the maximum molar absorptivity.

If we look at the spectra of $CuCl_3^-$, the situation is more complicated. $CuCl_3^-$ is believed to be solvated in dimethylformamide[12] and dimethyl sulfoxide[13] but only very weakly solvated in propylene carbonate.[13] An interesting phenomenon is that $CuCl_3^-$ in propylene carbonate exhibits a splitting of the near-infrared d–d transition band. The authors suggest that this is possibly due to the existence of two different configurations of $CuCl_3^-$. It is interesting to note that such a splitting is not found for $CuCl_3^-$ in KCl–AlCl$_3$. Perhaps the higher temperature in KCl–AlCl$_3$ favors only one of these configurations.

It is also interesting to note that, apart from the lack of the band at 9.3 × 10^3 cm^{-1}, the band positions and molar absorptivities in KCl–AlCl$_3$ and in propylene carbonate are in good agreement. By contrast, the band located around 26.3 cm^{-1} in dimethylformamide and dimethyl sulfoxide is not found in propylene carbonate or KCl–AlCl$_3$. This could be taken as an indication that no solvation takes place in the case of $CuCl_3^-$ in KCl–AlCl$_3$, and this is similar to what has been found to be the case for $NiCl_3^-$ in CsCl–AlCl$_3$[36] in the temperature range 500–750 °C.

Contrary to what is found for $CuCl_3^-$, $CuCl_2$ seems only to be found in an appreciable amount in propylene carbonate, whereas calculations in connection with Cu(II) in dimethylformamide[12] and dimethyl sulfoxide[13] indicate that $CuCl_2$ is probably not present to any large extent in these solvents. Furthermore, it seems very difficult to find any resemblance between the spectra of $CuCl_2$ in propylene carbonate and in KCl–AlCl$_3$, except perhaps for the band around 11.0 × 10^3 cm^{-1}. Both band locations and the molar absorptivities are very different in the two systems. The observed molar absorptivities for the charge-transfer bands of $CuCl_2$ in KCl–AlCl$_3$ are in fact lower than what is normally found for charge-transfer bands, indicating that this spectrum is to some extent due to transitions not allowed.

It is difficult to give explanation of this difference in band positions and molar absorptivities except that we must be dealing with rather dissimilar structures in the two cases.

One explanation could be that $CuCl_2$ in KCl–AlCl$_3$ (in contrast to $CuCl_2$ in propylene carbonate) is solvated. An example of such a solvated complex is the gas-phase complex, $CuAl_2Cl_8$, which can be looked upon as $CuCl_2$ solvated in Al_2Cl_6. However, a comparison between the band positions and molar absorptivities given in Table IX makes it rather unlikely that we are dealing with the same type of structure in the two cases. The spectrum of $CuAl_2Cl_8$ does not resemble the spectrum of $CuCl_2$ in KCl–AlCl$_3$, or any of the other spectra given in Table IX. This is in agreement with the proposed structures for $CuAl_2Cl_8$ (square planar or distorted octrahedron[17]), which are different from those expected in the other given solvents. A spectrum of the charge-transfer bands of $CuCl_2$ in the gas phase would of course also be interesting for comparison. However, sufficiently complete measurements are apparently not available at present.

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Registry No. $CuCl_2$, 7447-39-4; $AlCl_3$, 7446-70-0; KCl, 7447-40-7.