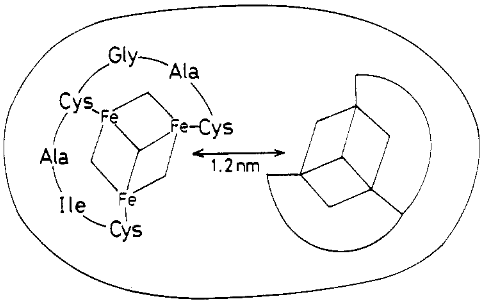

Figure 5. Chelation of Cys-Ile-Ala-Cys-Gly-Ala-Cys sequence to the $Fe_4S_4^{2+}$ cluster in *P. aerogenes* ferredoxin.[32]

The orientation is facilitated by the formation of the NH- - -S hydrogen bond and probably influences the strength of the Fe–S bond with the variation of S*–Fe–S–C torsion angles.

Role of Invariant Sequence around $Fe_4S_4^{2+}$ in Bacterial Ferredoxins. *P. aerogenes* ferredoxin has a characteristic sequence, Cys-Ile-Ala-Cys-Gly-Ala-Cys, which chelates in tridentate fashion to $Fe_4S_4^{2+}$. The first half of the sequence causes a negative shift of redox potential, but the later half tends to shift it positively. The remarkable difference of the redox potentials between **1** and **2** in dichloromethane suggests that a cluster of the native [4Fe-4S] ferredoxin has Fe ions with different environments, since a part of $Fe_4S_4^{2+}$ core is surrounded by Cys-Gly-Ala and the other by Cys-Ile-Ala sequences. The extremely positive shift of redox potential of **1** suggests that the peptide conformation of **1** in dichloromethane at low temperature (−40 °C) corresponds to a folding conformation of the later half (Cys-Gly-Ala-Cys), with NH- - -S hydrogen bonds that are supported by the hydrophobic side chains surrounding the peptide chain. Another hydrophobic peptide complex, $[Fe_4S_4(\text{Z-Cys-Pro-Val-OMe})_4]^{2-}$ having the sequence of the $Fe_4S_4^{2+}$ core of *P. aerogenes* ferredoxin, exhibits a relatively negative redox potential (−1.34 V vs. SCE in DMF).[34] An X-ray analysis of *P. aerogenes* ferredoxin by Adman et al.[32] indicates that the Cys-Ile-Ala-Cys sequence is located far from another $Fe_4S_4^{2+}$ core (cluster II) and the Cys-Gly-Ala-Cys sequence is between the two Fe_4S_4 cores while the Cys-Pro-Val sequence is on one side of cluster I as shown in Figure 5. Such an inequivalence within the $Fe_4S_4^{2+}$ core may play an important role in electron transfer, especially in influencing the direction of flow of electrons in biological electron-transfer chains.

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(34) Ueyama, N.; Kajiwara, A.; Terakawa, T.; Nakamura, A., manuscript in preparation.

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Potentiometric Study of the Solvent Equilibria in $AlCl_3$–*N*-*n*-Butylpyridinium Chloride Melts

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The solvent acid–base properties of acidic ($AlCl_3$-rich) $AlCl_3$–*N*-*n*-butylpyridinium chloride melts have been investigated by potentiometry for compositions up to 2.15:1 molar ratio $AlCl_3$:BuPyCl (the upper composition limit depends on the temperature). The ionic species distribution in this molten salt system is fully described by the following two equilibrium reactions: (I) $2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^-$; (II) $2Al_2Cl_7^- \rightleftharpoons Al_3Cl_{10}^- + AlCl_4^-$. Equilibrium I is shifted completely to the right (i.e. formation of $Al_2Cl_7^-$) in acidic melts. The value of the equilibrium constant K_{II} was determined as 2.09 (±0.06) × 10^{-3} (40 °C), 2.93 (±0.02) × 10^{-3} (60 °C), and 4.01 (±0.07) × 10^{-3} (80 °C); $\Delta H° = 15.20\ (\pm 0.28)$ kJ and $\Delta S° = -2.86\ (\pm 0.86)$ J/deg.

Introduction

Mixtures of aluminum chloride and *N*-*n*-butylpyridinium chloride (BuPyCl) are ionic liquids at ambient temperatures (the system is liquid below 27 °C over the composition range 0.75:1 to 2:1 molar ratio of $AlCl_3$:BuPyCl).[1,2]

Gale and Osteryoung[3] and, later, Schoebrechts and Gilbert[4] concluded from potentiometric measurements on concentration cells of the type

$$\text{Al|BuPyCl,AlCl}_3\text{(ref):fritted disk:AlCl}_3\text{,BuPyCl|Al} \qquad (1)$$

that the Lewis acid–base properties of this low-temperature molten salt can be represented by the single equilibrium reaction

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^- \qquad (I)$$

It is difficult to obtain accurate values of K_I from potentiometric measurements on concentration cells of type 1 because of the oxidation of aluminum metal by the organic cation in basic (chloride-rich) melts. The value of K_I deduced by Karpinski and Osteryoung[5] from voltammetric measurements, $\log K_I = -16.9$ (±2) at 40 °C, seems to be the more acceptable estimate (this value is several orders of magnitude smaller than the values determined by potentiometry[3,4]).

The conclusion that the single equilibrium reaction I provides an adequate description of the system throughout the entire range of melt compositions up to a 2:1 molar ratio of $AlCl_3$:BuPyCl seems to be supported by ^{27}Al NMR[6,7] and Raman[8] spectral results (none of the more intense Raman bands of liquid or gaseous aluminum chloride could be ascertained in the spectra, even in acidic ($AlCl_3$-rich) melts; this is consistent with the observation that sublimation losses of aluminum chloride are minimal even at high temperatures). Nevertheless, there are several reasons why it is necessary to consider additional equilibria, involving species such as $AlCl_3$, Al_2Cl_6, $Al_3Cl_{10}^-$ (which all are known to exist in inorganic chloroaluminates), for the most acidic melt compositions. Thus, systematic deviations are observed between the experimental and theoretical potentials, increasing with the melt acidity for compositions higher than ~1.8:1 molar ratio of $AlCl_3$:BuPyCl, if the theoretical potentials are calculated on the

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(1) Robinson, J.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 303.
(2) Hussey, C. L. *Adv. Molten Salt Chem.* **1983**, *5*, 185.
(3) Gale, R. J.; Osteryoung, R. A. *Inorg. Chem.* **1979**, *18*, 1603.
(4) Schoebrechts, J. P.; Gilbert, B. P. *J. Electrochem. Soc.* **1981**, *128*, 2679.
(5) Karpinski, Z. J.; Osteryoung, R. A. *Inorg. Chem.* **1984**, *23*, 1491.
(6) Gray, J. L.; Maciel, G. E. *J. Am. Chem. Soc.* **1981**, *103*, 7147.
(7) Wilkes, J. S.; Reynolds, G. F.; Frye, J. S. *Inorg. Chem.* **1983**, *22*, 3870.
(8) Gale, R. J.; Gilbert, B.; Osteryoung, R. A. *Inorg. Chem.* **1978**, *17*, 2728.

0020-1669/85/1324-4704$01.50/0 © 1985 American Chemical Society

basis of the single equilibrium reaction (I).[4] Furthermore, it is obvious that a model involving only the single equilibrium reaction I is totally inappropriate to describe the solvent acid-base properties of melts with molar ratio of $AlCl_3$:BuPyCl $\geqslant$ 2:1.

This paper reports the results of potentiometric measurements on concentration cells (1) for melt compositions up to a 2.15:1 molar ratio of $AlCl_3$:BuPyCl (the upper composition limit depends on the temperature). The results are interpreted by the formation of $Al_3Cl_{10}^-$ (the most likely higher complex after $Al_2Cl_7^-$) in this low-temperature molten salt system.

Experimental Section

The method of Robinson and Osteryoung[1] was used for the synthesis and purification of *N-n*-butylpyridinium chloride and the sublimation of aluminum chloride (Fluka, iron-free). The most important single factor for the preparation of colorless melts is the careful synthesis of *N-n*-butylpyridinium chloride, as was noted earlier by Schoebrechts and Gilbert.[4] The melts were prepared by adding the crystals of aluminum chloride slowly, with vigorous stirring, to the crystals of *N-n*-butylpyridinium chloride: this procedure is essential to avoid thermal decomposition and discoloration of the melts.

The preparation of the melts and all subsequent titrations were carried out under a purified nitrogen atmosphere (VAC drybox; HE-493 Dri Train). The temperature of the melts was controlled (±0.5 °C) by circulating oil, from a thermostat outside the drybox, through the jacket of the Pyrex cell used for the potentiometric measurements. The reference electrode compartment contained melt with a known composition (usually close or equal to a 2:1 molar ratio of $AlCl_3$:BuPyCl) and was separated from the melt by a fine-porosity glass frit. The indicator and reference electrodes, coiled aluminum wires (Alfa Inorganics; m5N) were digested for 24 h in an acidic melt before use. Potentiometric titrations were performed by successive additions of accurately weighed (±0.1 mg) portions of *N-n*-butylpyridinium chloride to the melts; rather large amounts of melt (60–100 g) were used for each experiment in order to minimize the accumulation of weighing errors during the titration. Potentials were measured (±0.1 mV) with a Beckman Model 4500 digital pH meter.

Results and Discussion

The electrode reaction at an aluminum indicator electrode in chloroaluminate melts can be written as

$$AlCl_4^- + 3e^- \rightleftharpoons Al + 4Cl^- \tag{2}$$

Using the Nernst equation and taking into account the equilibrium reaction (I), the potential for cell 1 is given by

$$E = \frac{7RT}{3F}\ln\frac{[AlCl_4^-]_{\mathrm{ref}}}{[AlCl_4^-]} + \frac{4RT}{3F}\ln\frac{[Al_2Cl_7^-]}{[Al_2Cl_7^-]_{\mathrm{ref}}} \tag{3}$$

where square brackets denote mole fractions. The liquid-junction potential across the fritted glass disk is neglected in this expression: the justification to do so was provided by recent experimental work of Hussey and Øye,[9] who determined transport numbers in room-temperature chloroaluminate melts and found that the internal transport number of the organic cation is unity in acidic melts.[10] Furthermore, the activity coefficients of all the species in the melt are assumed to be unity in all the calculations in this work.

For acidic melts, the reaction $AlCl_4^- + AlCl_3 \rightleftarrows Al_2Cl_7^-$ is shifted completely to the right, and therefore, if only this equilibrium is considered, $[AlCl_4^-] \simeq (1 - X)$ and $[Al_2Cl_7^-] = X$ (see Appendix, eq 6A and 7A; the composition of the melt is defined by 1 mol of $BuPyAlCl_4$ + X mol of $AlCl_3$). Evidently, the potential for cell 1 is then determined only by the composition of the melts and can be easily calculated. A comparison between the calculated and the experimental potentials is shown in Figure 1 for the titration of a melt with a 2:1 molar ratio of $AlCl_3$:BuPyCl composition at 40 °C (in this figure, the potentials were adjusted to an uncommon reference electrode—aluminum in a melt with a 1.5:1 molar ratio of $AlCl_3$:BuPyCl composition—for the obvious reason that eq 3 is undefined for $X \geqslant 1$ if only the single equilibrium reaction I is considered). The agreement between the calculated and the experimental potentials is excellent up to ~1.8:1 molar ratio of $AlCl_3$:BuPyCl but systematic deviations are observed for the more acidic melt compositions.[12] Therefore, a second equilibrium reaction involving the formation of the $Al_3Cl_{10}^-$ ion

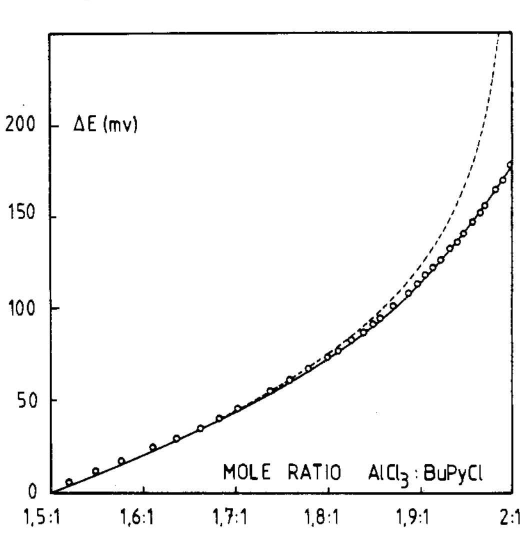

Figure 1. Potentiometric titration of an acidic $AlCl_3$–*N-n*-butylpyridinium chloride melt at 40 °C (reference electrode compartment: 1.5:1 molar ratio of $AlCl_3$:BuPyCl): open circles, experimental data; broken line, theory (equilibrium I); full line, theory (combination of equilibria I and II).

$$2Al_2Cl_7^- \rightleftharpoons Al_3Cl_{10}^- + AlCl_4^- \tag{II}$$

was included in the calculations (see Appendix). The rationale to consider an equilibrium involving $Al_3Cl_{10}^-$, rather than $AlCl_3$ or Al_2Cl_6, can be summarized as follows:

(i) The equilibrium constant K_0 for reaction $2AlCl_3(l) \rightleftarrows Al_2Cl_6(l)$ can be calculated by using the procedure outlined by King et al.:[13] extrapolation of the available data[14] to room temperature yields $K_0 \simeq 1.5 \times 10^{11}$ at 40 °C, indicating that this equilibrium is shifted completely to the right (i.e. formation of the dimeric species). Therefore, only Al_2Cl_6 needs to be considered if neutral aluminum chloride species are included in the calculations.

(ii) It is impossible to fit the experimental data by a combination of the two reactions $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$ (I) and $2AlCl_4^- + Al_2Cl_6 \rightleftarrows 2Al_2Cl_7^-$.

(iii) The existence of a polymeric species higher than $Al_2Cl_7^-$ in acidic aluminum chloride–alkali-metal chloride melts is supported by Raman spectroscopic evidence.[15-17]

The combination of equilibria I and II gives an excellent fit of the experimental data over the whole composition range of acidic

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[9] Hussey, C. L.; Øye, H. A. *J. Electrochem. Soc.* **1984**, *131*, 1621.

[10] Øye and King[11] published a rigorous thermodynamic analysis of chloroaluminate concentration cells and argued that the concept of liquid-junction potentials is unnecessary and should be avoided as it leads to an artificial division of electrode and junction processes by introduction of an undefined single-ion potential. However, with $t_{\mathrm{BuPy^+}} = 1$, their expression for the emf reduces to $-F\mathrm{d}E = {}^1/_3\mathrm{d}\mu_{AlCl_4^-} - {}^4/_3\mathrm{d}\mu_{Cl^-}$, which is identical with eq 3.

[11] Øye, H. A.; King, L. A. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 547.

[12] Schoebrechts and Gilbert[4] attributed these deviations to the fact that the liquid-junction potential was neglected in their calculations and obtained a much better agreement between the experimental and calculated potentials if a correction was made for the junction potential (which was calculated by using some simple assumptions concerning the ionic mobilities). However, as noted already, Hussey and Øye[9] have shown that the junction potential can be effectively neglected in acidic melts.

[13] Fannin, A. A.; King, L. A.; Seegmiller, D. W. *J. Electrochem. Soc.* **1972**, *119*, 801.

[14] Boxall, L. G.; Jones, H. L.; Osteryoung, R. A. *J. Electrochem. Soc.* **1973**, *120*, 223.

[15] Torsi, G.; Mamantov, G.; Begun, G. M. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 553.

[16] Øye, H. A.; Rytter, E.; Klaeboe, P.; Cyvin, S. J. *Acta Chem. Scand.* **1971**, *25*, 559.

[17] Rytter, E.; Øye, H. A.; Cyvin, S. J.; Cyvin, B. N.; Klaeboe, P. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1185.

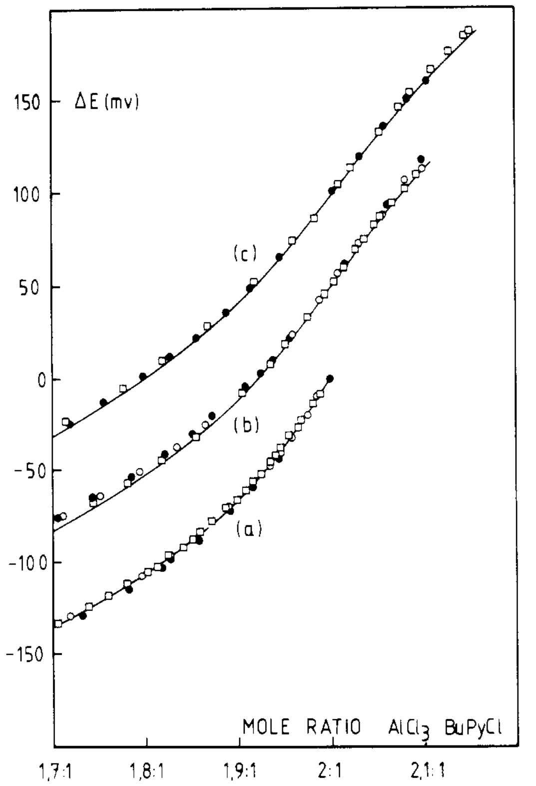

Figure 2. Potentiometric titration of acidic $AlCl_3$–*N*-*n*-butylpyridinium chloride melts at different temperatures (reference electrode compartment: 2:1 molar ratio of $AlCl_3$:BuPyCl): a, 40 °C; b, 60 °C (the curve is shifted upward by 50 mV); c, 80 °C (the curve is shifted upward by 100 mV). Full lines were calculated by using the K_{II} values given in Table I.

Table I. Mole Fraction Equilibrium Constant and Thermodynamic Constants for the Reaction $2BuPyAl_2Cl_7 \rightleftharpoons BuPyAlCl_4 + BuPyAl_3Cl_{10}$[a]

T, °C	40	60	80
10^3K_{II}	2.09 (±0.06)	2.93 (±0.02)	4.01 (±0.07)

$\Delta H° = 15.20\ (\pm 0.28)$ kJ
$\Delta S° = -2.86\ (\pm 0.86)$ J/deg

[a] The values of the equilibrium constant were determined from three independent titration experiments for each temperature.

melts at 40 °C as is shown in Figure 2 (the standard deviation in the potential—for a definition, see appendix—is less than 1 mV for each independent titration experiment). Titration curves obtained at 60 and 80 °C for 2.1:1 and 2.15:1 molar ratios of $AlCl_3$:BuPyCl respectively are also shown in this figure: the agreement between the experimental and the calculated potentials is again excellent. At these higher temperatures, melts with a molar ratio of $AlCl_3$:BuPyCl in excess of 2:1 could be easily prepared although the melts slightly discolored after the prolonged heating necessary for the complete dissolution of the aluminum chloride crystals. The phase diagram of the $AlCl_3$–*N*-*n*-butylpyridinium chloride system is not known, and no attempt was made in this work to determine the maximum solubility of aluminum chloride in acidic melts at different temperatures. However, the phase diagrams of the similar $AlCl_3$–*N*-ethylpyridinium bromide[18] and $AlCl_3$–1-methyl-2-ethylimidazolium chloride[19] systems show a steep increase of the liquidus temperature for melt compositions in excess of a 2:1 molar ratio of $AlCl_3$:MCl (where M is the organic cation), which makes it reasonable to assume that the most acidic melt compositions used in this work are actually close to the maximum solubility of aluminum chloride in these melts.[20]

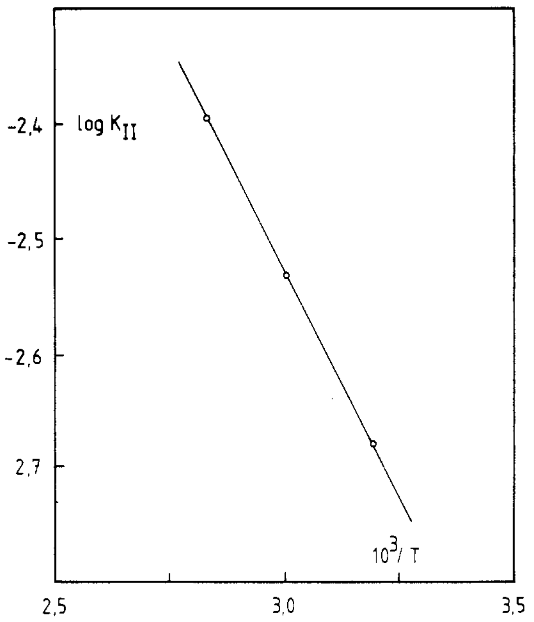

Figure 3. Plot of log K_{II} as a function of the inverse absolute temperature (the straight line is drawn from a least-squares calculation).

The values of the equilibrium constant K_{II} at different temperatures were determined from a variance analysis of the experimental titration curves and are given in Table I (a titration curve covering the whole range of acidic melt compositions was recorded in each experiment but only the data points for the molar ratio of $AlCl_3$:BuPyCl $\geq$ 1.8:1 were used to determine the K_{II} values). A plot of log K_{II} as a function of the inverse of the absolute temperature is shown in Figure 3 and yields $\Delta H° = 15.20$ (±0.28) kJ and $\Delta S° = -2.86$ (±0.86) J/deg. The relatively low value of the entropy change reflects the fact that the number of degrees of freedom, translational and vibrational, remains virtually unchanged in the reaction. The fact that the potentiometric curves in acidic melts are rather insensitive to temperature variations was observed previously by Gale and Osteryoung.[3]

The main evidence for the existence of $Al_3Cl_{10}^-$ in acidic aluminum chloride–alkali-metal chloride melts was derived from Raman spectral results.[15-17] Most workers who investigated the solvent equilibria in the inorganic melt systems by potentiometric methods did not include equilibria involving $Al_3Cl_{10}^-$ in their calculations. Fannin et al.[13] considered, inter alia, the equilibria

$$AlCl_4^- + AlCl_3 \rightleftharpoons Al_2Cl_7^- \qquad \text{(III)}$$

$$Al_2Cl_7^- + AlCl_3 \rightleftharpoons Al_3Cl_{10}^- \qquad \text{(IV)}$$

in $AlCl_3$–NaCl melts and reported $K_{III} = 2.5 \times 10^4$ and $K_{IV} \leq 10^3$ or, since $K_{II} = K_{IV}/K_{III}$, $K_{II} \leq 4 \times 10^{-2}$ at 175 °C. Extrapolation of the data reported in this paper to the same temperature yields $K_{II} \simeq 1.2 \times 10^{-2}$, i.e., a value of the same order of magnitude as the upper limit estimated for $AlCl_3$–NaCl melts.[22] It

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(18) Hurley, F. H.; Wier, T. P. *J. Electrochem. Soc.* **1951**, *98*, 203.

(19) Landers, J. S.; Stech, D. J.; Wilkes, J. S., Frank J. Seiler Research Laboratory, USAF Academy, Colorado Springs, CO, unpublished data cited in ref 2.

(20) Matsumoto and Ichikawa[21] reported the results of ^{27}Al NMR measurements at 45 °C for acidic melt compositions up to 80 mol % $AlCl_3$ (molar ratio $AlCl_3$:BuPyCl = 4!). In this laboratory, it was found impossible to cover such a large composition range at this relatively low temperature. Incidentally, these authors claimed evidence for the fact that $Al_3Cl_{10}^-$ becomes dominant over $Al_2Cl_7^-$ in their most acidic melts.

(21) Matsumoto, T.; Ichikawa, K. "Proceedings of the First International Symposium on Molten Salt Chemistry and Technology", Kyoto, Japan, 1983; p 383.

(22) Brekke et al.[23] considered a combination of two reactions, $2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^-$ (I) and $3Al_2Cl_7^- \rightleftharpoons 2Al_3Cl_{10}^- + Cl^-$ (V), to describe the solvent equilibria in $AlCl_3$–KCl melts at 275–350 °C. Obviously, $K_{II} = (K_V/K_I)^{1/2}$, and insertion of their numerical data yields $K_{II} \simeq 1.9$ and 1.1 at 275 and 350 °C, respectively, i.e. values that seem improbably high. It must be noted however that their values of the equilibrium constants were deduced from potentiometric measurements over a rather small range of melt compositions close to a 1:1 molar ratio of $AlCl_3$:KCl, and therefore, it is not surprising that other model equilibria did fit the data equally well.

must be born in mind however that it is difficult to compare the absolute values of equilibrium constants for different chloroaluminate melts because of the large cation effect on the solvent acid–base equilibria.[24] Thus, Gale and Osteryoung[3] postulated that the increased extent of $Al_2Cl_7^-$ ion formation in room-temperature chloroaluminates, as compared to the inorganic systems, results from the decreased polarizing power of the organic cation. By the same argument, the large size of the organic cation can be expected to enhance the formation of the $Al_3Cl_{10}^-$ anion, but a comparison with other systems is impossible for lack of experimental data.

Conclusion

In conclusion, the results of this paper show that the solvent equilibria in acidic $AlCl_3$–*N*-*n*-butylpyridinium chloride melts are adequately represented by the combination of two equilibria, (I) and (II). Obviously it would be interesting to confirm the conclusions of this work directly by Raman spectroscopic studies on very acidic melts (molar ratio of $AlCl_3$:BuPyCl > 2:1), where the mole fraction of $Al_3Cl_{10}^-$ becomes appreciable. The results obtained thus far by this technique in this laboratory are inconclusive because of the poor quality of the spectra in acidic melts (as was also noted earlier[8]). Finally, the results of this work allow a precise calculation of the pCl values over the whole composition range of acidic melts, at least on a relative scale: the absolute value of the pCl depends of course also on the value of K_I, which is not known with sufficient accuracy. Fortunately, for most practical applications, the variation of pCl with the melt composition is the more important factor.

Acknowledgment. The authors wish to acknowledge the assistance of S. Raman during the experimental portion of this study. This work was supported by the Interuniversitair Instituut voor Kernwetenschappen (IIKW), Brussels, Belgium.

Appendix

The composition of the melt is defined by 1 mol of $BuPyAlCl_4$ + *X* mol of $AlCl_3$ (the mole fraction of aluminum chloride, more commonly used to represent the composition of these melts, is then given by $(1 + X)/(2 + X)$). The mass balances for aluminum and chlorine are given by

$$(AlCl_4^-) + 2(Al_2Cl_7^-) + 3(Al_3Cl_{10}^-) = 1 + X \qquad (1A)$$

$$4(AlCl_4^-) + 7(Al_2Cl_7^-) + 10(Al_3Cl_{10}^-) + (Cl^-) = 4 + 3X \qquad (2A)$$

where $(AlCl_4^-)$ is the number of moles of $BuPyAlCl_4$ in the system, etc. It follows at once that

$$(AlCl_4^-) = 1 - X + (Al_3Cl_{10}^-) - 2(Cl^-) \qquad (3A)$$

$$(Al_2Cl_7^-) = X - 2(Al_3Cl_{10}^-) + (Cl^-) \qquad (4A)$$

Furthermore, the total number of moles in the system is given by

$$T = (AlCl_4^-) + (Al_2Cl_7^-) + (Al_3Cl_{10}^-) + (Cl^-) = 1 \qquad (5A)$$

so that $[AlCl_4^-] = (AlCl_4^-)/T$, etc., where square brackets denote mole fractions. In acidic melts, the mole fraction of chloride ions can be neglected in the mass balances so that

$$[AlCl_4^-] = 1 - X + [Al_3Cl_{10}^-] \qquad (6A)$$

$$[Al_2Cl_7^-] = X - 2[Al_3Cl_{10}^-] \qquad (7A)$$

Substitution of these equations into the expression for the mole fraction equilibrium constant K_{II} yields a quadratic equation

$$(1 - 4K_{II})[Al_3Cl_{10}^-]^2 + [1 - X(1 - 4K_{II})][Al_3Cl_{10}^-] - K_{II}X^2 = 0 \qquad (8A)$$

which can be solved to give

$$[Al_3Cl_{10}^-] = \{-[1 - X(1 - 4K_{II})] + ([1 - X(1 - 4K_{II})]^2 + 4K_{II}X^2(1 - 4K_{II}))^{1/2}\}/2(1 - 4K_{II}) \qquad (9A)$$

(obviously, this equation can be further simplified if the condition $4K_{II} <<1$ is fulfilled). The potential of cell 1 can then be calculated by using eq 3 after substitution of eq 9A in eq 6A and 7A. The value of the equilibrium constant for reaction II was calculated by varying the K_{II} value to obtain a minimum standard deviation E_{SD} between the experimental and calculated potentials, where the standard deviation of the potential is given by

$$E_{SD} = ([\sum_{i=1}^{D}(E_{i,\mathrm{theor}} - E_{i,\mathrm{exptl}})^2]/(D - 1))^{1/2} \qquad (10A)$$

where *D* is the number of data points. The values of the equilibrium constant given in Table I are the mean values obtained from at least three independent titrations for each temperature. The experimental potential values of the independent titration experiments were adjusted to one common reference electrode (aluminum in a melt with a 2:1 molar ratio of $AlCl_3$:BuPyCl composition) for the sake of clarity of the graphical representation of the data.

Registry No. BuPyCl, 1124-64-7; $AlCl_3$, 7446-70-0; $AlCl_4^-$, 17611-22-2; $Al_2Cl_7^-$, 27893-52-3; $Al_3Cl_{10}^-$, 37233-70-8.

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Mechanism of the Water-Mediated Reduction of Tris(2,2′-bipyridine-*N*,*N*′)iron(III), -ruthenium(III), and -osmium(III) Complexes

Peter A. Lay* and Wolfgang H. F. Sasse

Received November 27, 1984

A new mechanism is proposed for the reduction of $[M(bpy)_3]^{3+}$ (bpy = 2,2′-bipyridine) ions by water. The initial step in the reaction is nucleophilic attack of a water molecule (or OH^-) at the metal center to form a seven-coordinate intermediate. This intermediate may undergo oxidation by another molecule of $[M(bpy)_3]^{3+}$ to give a seven-coordinate M(IV)–oxo species and $[M(bpy)_3]^{2+}$. Subsequent ligand loss and/or oxidation follows. Dioxygen evolution results from the formation of binuclear oxo complexes, which act as catalysts (in the presence of $[M(bpy)_3]^{3+}$) for the oxidation of water to dioxygen.

Dioxygen evolution from $[M(bpy)_3]^{3+}$ ions (bpy = 2,2′-bipyridine) is of particular interest in the area of solar energy research, since the Ru(III) complex is produced during the photoreduction of water to H_2 using $[Ru(bpy)_3]^{2+}$ as sensitizer.[1] The kinetics of the reduction of $[Fe(bpy)_3]^{3+}$ and $[Ru(bpy)_3]^{3+}$ by water have been studied in great detail,[2-7] but there is no

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