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Electrochemical and Spectral Investigations of Nickel(II) Ion Equilibria in Room-Temperature Chloroaluminate Solvents

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Absorption spectra have been recorded for $NiCl_2$ dissolved in 0.8:1 and 1.5:1 molar ratio $AlCl_3$–1-butylpyridinium chloride at room temperature. In basic (chloride-rich) melts, the Ni(II) is present as $NiCl_4^{2-}$, with molar extinction coefficients $a_{658} = 169$ and $a_{705} = 175$ L mol^{-1} cm^{-1}. The reduction of the Ni(II) ion species at vitreous carbon electrodes exhibited irreversible behavior in acidic melts, but no $NiCl_4^{2-}$ ion reduction was detected in the basic solvent. Potentiometry gave a theoretical two-electron Nernst slope for Ni(II) additions in the acidic region and a fourth-power Cl^- ion dependence consistent with $NiCl_4^{2-}$ formation in the basic region. At 40 °C, the Ni(0)/Ni(II) standard electrode potential on the mole fraction scale was determined to be $+0.800 \pm 0.005$ V (vs. a 2:1 Al reference), and an equilibrium constant for the dissociation reaction $NiCl_4^{2-} \rightleftarrows Ni^{2+} + 4Cl^-$ was determined to be $(1.2 \pm 1.0) \times 10^{-46}$.

Introduction

Certain molten salt mixtures of aluminum chloride and alkylpyridinium halides are liquid at ambient temperatures in a broad compositional range, thereby providing unusual ionic solvents for studies of acid–base chemistry, ion complexation, electrochemically generated organic compounds, etc. (e.g., see ref 1–4). A potentiometric investigation of the aluminum species equilibria in $AlCl_3$–1-butylpyridinium chloride (1-BPC) melts[1] has established that the equilibrium constant for solvolysis reaction 1 has a value of $K_3 \lesssim 3.8 \times 10^{-13}$ at 30 °C,

$$2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^- \qquad (1)$$

the limit arising because the 1-butylpyridinium cation is spontaneously reduced by elemental aluminum in the basic composition range (i.e., <1:1 $AlCl_3$–1-BPC). The extent of formation of the $Al_2Cl_7^-$ ionic species was found to be decidedly enhanced in $AlCl_3$–1-BPC melts over that existing in the higher temperature $AlCl_3$–alkali metal chloride systems for a particular temperature. Additionally, the main disadvantage of the high Al_2Cl_6 vapor pressure found with the acidic $AlCl_3$–alkali metal chloride systems seems to be negated in the corresponding organic halide melts. Further substantiation of these conclusions has come from potentiometric studies made with a metal which is not capable of reducing the pyridinium cation, namely, nickel. Gilbert and Osteryoung[5] have investigated the electrochemistry of Ni(II) species in the $NaAlCl_4$ melt at temperatures between 175 and 210 °C. The Ni(II) standard potential at 175 °C in a melt of pCl^- 5.8 was found to be $E_0 = 1.433 \pm 0.002$ V vs. an Al reference (NaCl saturated). de Fremont et al.[6] have reported a half-wave potential value for Ni(II) ion reduction ($E_{1/2} = +0.83$ V vs. an Al reference (60:26:14)) in the eutectic fused salt $AlCl_3$–NaCl–KCl (60:26:14 mol %) at 140 °C and have found that Ni(II), Co(II), and Fe(II) ion reductions at the DME are irreversible, with a cathodic transfer coefficient for Ni(II) of $\alpha = 0.88$. The Ni–$NiCl_2$ electrode has been tried as a cathode for a solid-electrolyte battery, at operating temperatures of 600–1000 °C.[7]

Results and Discussion

Absorption Spectra. Anhydrous $NiCl_2$ was soluble in basic (<1:1 $AlCl_3$–1-BPC) and, with difficulty, in acidic (>1:1 $AlCl_3$–1-BPC) melts, the basic solutions being sea green/blue and the acidic solutions sandy colored. A light colored precipitate sometimes formed when the acidic melts were allowed to stand. Figure 1a illustrates the optical absorption spectrum of a dilute solution of $NiCl_2$ dissolved in a 0.8:1 melt at room temperature. The spectrum appears to be intermediate to those obtained from $NiCl_4^{2-}$ ions dissolved in pyridinium chloride at 160 °C and that obtained from those ions present as a solid solution in Cs_2ZnCl_4 at room temperature.[8] Absorption spectra of nickel ionic species in molten chloride media have been studied extensively[8-11] and, on the basis of these data, an unambiguous assignment for the spectrum in Figure 1a to a (approximately) tetrahedrally coordinated tetrachloronickelate ion species is possible. The most intense absorption doublet at 705 and 658 nm and the shoulder at ~617 nm (Figure 1a) have been assigned to the spin-allowed absorption $^3T_1(F)$ $^3T_1(P)$.[8-10] For the $NiCl_2$ composition range 1×10^{-3} to 1×10^{-2} M, the Bouger–Beer law was obeyed within experimental error, and molar extinction coefficients for the 658- and 705-nm band maxima computed from the least-squares straight lines were 169 and 175 L mol^{-1} cm^{-1}, respectively. These molar absorptivities are consistent with those of Smith, Liu, and Griffiths[9] for $NiCl_2$/tri-1-butylbenzylphosphonium chloride systems. They reported that increasing temperature (22–172 °C) caused a blue shift in the band maxima and a decrease in absorbance values such that at room temperatures $A_{707} > A_{660}$, whereas both maxima had the same a value of 156 L mol^{-1} cm^{-1} at 172 °C.

Figure 1b illustrates the spectrum of $NiCl_2$ dissolved in an acidic melt; a weak band at ~547 nm was the only band detected in the 400–800-nm spectral range. Øye and Gruen[12] have studied the absorption spectra of dipositive nickel in molten Al_2Cl_6 at 227 °C and 5.6 atm. The spectrum exhibited bands at 476, 926, and 1563 nm which have been interpreted in terms of octahedral coordination of chlorides about the central metal ion. Temperature-dependent equilibria involving

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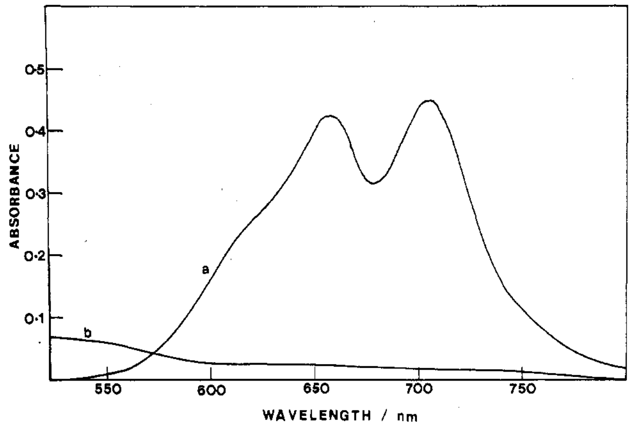

Figure 1. Absorption spectra of $NiCl_2$ dissolved in (a) a 0.8:1 $AlCl_3$-1-BPC melt ($[NiCl_2] = 2.7 \times 10^{-3}$ M) and (b) a 1.5:1 $AlCl_3$-1-BPC melt (nominal $[NiCl_2] = 1.23 \times 10^{-4}$ M) at room temperature.

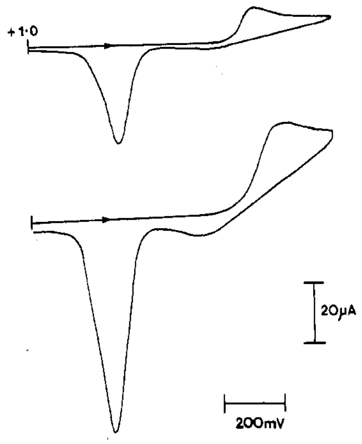

Figure 2. Cyclic voltammetry of Ni(II) in a 1.5:1 melt at 40 °C at a vitreous C electrode (area = 0.0855 cm^2). Sweep rates: upper, 20 mV s^{-1}; lower, 200 mV s^{-1}. Nickel mole fraction = 2.04×10^{-3}, added as $NiCl_2$.

both tetrahedral and octahedral states have been investigated[11] in LiCl–KCl mixtures at 400–700 °C, and an absorption band at 448 nm was assigned to Ni(II) in an octahedral site. Absorption band assignments have also been made for Ni(II) chloride species ($NiCl^+$, $NiCl_2$, $NiCl_3^-$, $NiCl_4^{2-}$) and the $Ni(Me_2SO)_6^{2+}$ octahedral cation in dimethyl sulfoxide solutions.[13] None of these peaks correlates to the one found for Ni(II) in the acidic $AlCl_3$–1-BPC melt at room temperature. This result could be consistent with the supposition that divalent nickel ion is in an uncomplexed state or perhaps only very weakly solvated in the acidic solvent (vide infra).

Electrochemical Behavior of Nickel(II). Figure 2 illustrates cyclic voltammograms obtained from solutions of $NiCl_2$ in acidic melts. The cathodic current peak for nickel deposition at ~+0.3 V vs. an Al(0) 2:1 melt reference shifts negative with increasing scan rate at 40 °C, which is diagnostic of a slow charge-transfer reaction rate (irreversible behavior). Unlike the high-temperature case,[5] the reverse scan produces a small anodic wave at ~+0.44 V, comprising ~7% of the total cathodic charge and preceding the bulk stripping peak at ~+0.7 V. The small peak may be due to codeposited aluminum in the nickel electrodeposit because of the proximity of the nickel species reduction to background aluminum reduction (~−0.15 V on vitreous C).

In basic melts at vitreous C electrodes, no wave for $NiCl_4^{2-}$ anion reduction appeared within the accessible solvent potential limits. This behavior is contrary to that found in organic solvents such as acetonitrile or dimethylformamide.[14,15]

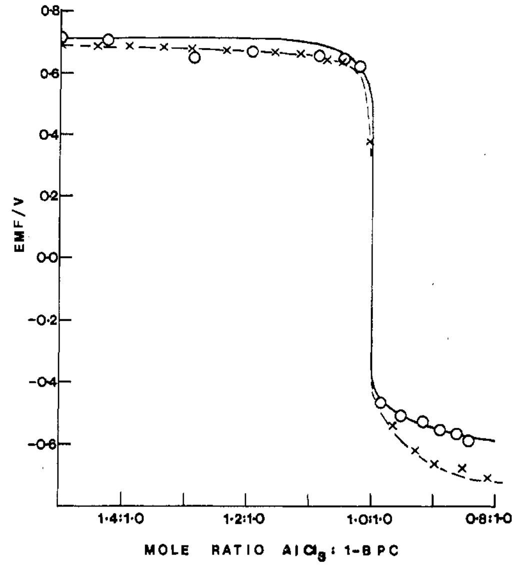

Figure 3. Potentiometric titration of Ni(II) by addition of 1-BPC: (○) 40 °C; (×) 150 °C.

Florence[14] has reported a well-defined polarographic wave ($E_{1/2} = -0.400$ V vs. SCE) in methanolic lithium chloride solutions with the $NiCl_4^{2-}$ complex ion as the predominant Ni(II) species. Similarly, Ciana and Furlani[15] have studied the polarographic behavior of $NiCl_4^{2-}$ ion in DMF and proposed that the nickel species reduction is preceded by rapid dissociation of the tetrahalogeno complex to the halide-free ion. The slowness of the rate of conversion to the electroactive form may explain the lack of $NiCl_4^{2-}$ species reduction in the basic, room-temperature solvent.

Equilibria Studies. In order to determine the standard reduction potential E_0, we obtained a Nernst plot by varying the nickel ion concentration in a 1.5:1 acidic melt and measuring the emf of a nickel electrode vs. an Al reference electrode. For the nickel ion mole fraction range 1.5×10^{-5} to 2.0×10^{-3}, the least-squares slope was calculated to be 31 mV (theory value $RT/2F$ at 40 °C is 31 mV) and the intercept value for the standard electrode potential on the mole fraction scale $E_0 = +0.800 \pm 0.005$ V vs. an Al reference. The activity of Ni(II) ion is assumed to be equal to the added Ni(II) concentrations. It may be noted that in the acidic composition range [(1.5–1.1):1 molar ratio] the nickel ion potential is practically unaffected by the melt acidity (Figure 3), despite relative changes in the $AlCl_4^-$, $Al_2Cl_7^-$, and Cl^- ion concentrations.

Emf measurements have been made between a nickel working electrode and an Al reference electrode as a function of the melt composition, and typical data are illustrated in Figure 3. On the basis of the absorption spectroscopy results, it may be assumed that the major nickel ion equilibrium reaction in the basic melts can be represented by the formation of a single halonickel complex ion, $NiCl_4^{2-}$

$$Ni^{2+} + 4Cl^- \rightleftarrows NiCl_4^{2-} \tag{2}$$

The potentiometric curve may then be expressed approximately by relationship 3 in which the species activities have been

$$E = E_0 + \frac{RT}{2F} \ln [NiCl_4^{2-}] + \frac{RT}{2F} \ln K - \frac{RT}{2F} \ln [Cl^-]^4 \tag{3}$$

replaced by concentrations and the equilibrium constant K is defined by

$$K = [Ni^{2+}][Cl^-]^4/[NiCl_4^{2-}] \tag{4}$$

The nickel ion concentrations in the basic composition range

Table I. Ion Mole Fractions and Equilibrium Constants for Titration of 2.04×10^{-3} M $NiCl_2$ in a 1.5:1 Melt at 40 °C

emf, V	Ni^{2+} [a]	Cl^- ion in excess to 1:1	$NiCl_4^{2-}$	Cl^- [b]	*K*
−0.464	2.15×10^{-41}	8.57×10^{-3}	1.72×10^{-3}	1.69×10^{-3}	1.02×10^{-49}
−0.504	1.11×10^{-42}	2.56×10^{-2}	1.75×10^{-3}	1.86×10^{-2}	7.59×10^{-47}
−0.524	2.51×10^{-43}	4.38×10^{-2}	1.78×10^{-3}	3.67×10^{-2}	2.56×10^{-46}
−0.551	3.40×10^{-44}	5.93×10^{-2}	1.80×10^{-3}	5.21×10^{-2}	1.39×10^{-46}
−0.560	1.74×10^{-44}	7.47×10^{-2}	1.83×10^{-3}	6.74×10^{-2}	1.96×10^{-46}
−0.586	2.54×10^{-45}	8.58×10^{-2}	1.85×10^{-3}	7.84×10^{-2}	5.19×10^{-47}

[a] Calculated from the Nernst equation. [b] Cl^- ion fraction excess minus Cl^- combined with Ni(II).

can be calculated at each of the measured emf values from the Nernst equation (eq 5), provided that the standard

$$E = E_0 + \frac{RT}{2F} \ln a_{\mathrm{Ni}}{}^{2+} \qquad (5)$$

electrode pontential is known. As the mole fraction of chloride ions is the excess of 1-BPC—that in excess of the 1:1 molar ratio minus that combined with the Ni(II)—a mean equilibrium constant for eq 2 could be calculated for the basic datum points, $\bar{K} = (1.2 \pm 1.0) \times 10^{-46}$ (40 °C). Table I contains representative calculations of the ion fractions.

From the equilibrium constant, it is possible to determine the chloride ion concentration at the equivalence midpoint of the potential break and to determine the equilibrium constant K_3 for the aluminum ion species equilibria. At the midpoint, $E_e = +0.080$ V, $[Ni^{2+}]_e = 6.71 \times 10^{-24}$, $[NiCl_4^{2-}] = 1.70 \times 10^{-3}$, and $[Cl^-]_e = 4.18 \times 10^{-7}$. When the mass balance relationship at the equivalence point ($[Al_2Cl_7^-]_e = [Cl^-]_e$ is used and K_3 is defined as

$$K_3 = [Al_2Cl_7^-][Cl^-]/[AlCl_4^-]^2 \qquad (6)$$

the equilibrium constant becomes $K_3 = 1.74 \times 10^{-13}$, in reasonable agreement with the values reported earlier ($K_3 \lesssim 9.5 \times 10^{-13}$ for 40 °C and ideal behavior.[1]) The model assumes that the tetrachloronickelate ion is the major Ni(II) chloride species in the equivalence region. For the basic emf values at 55 °C, a graph of emf vs. log $[Cl^-]$ gave a straight line of slope 0.135 ± 0.011 V and a correlation coefficient of 0.995, in agreement with the theoretical slope of 0.130 V for a fourth-power dependence on chloride ion concentration. The standard free energy of formation of the tetrachloronickelate anion may be calculated from the equilibrium constant, at 40 °C: $\Delta G^\circ = -RT \ln K = 274$ kJ mol^{-1}. Assuming that this model is appropriate at higher temperatures, we determined from potentiometric titration curves that the ΔG° values at 120 and 150 °C were 291 and 304 kJ mol^{-1}, respectively. The standard state for these calculations is Ni(II) ion in the acidic melt, and there does not appear to be any comparative thermodynamic data for $NiCl_4^{2-}$ ion formation in the literature on molten salts. However, it is well-known that transition-metal–halogen complexes of symmetry T_d do have appreciable stability in polar organic solvents in the absence of water.[13,15]

Conclusions

Consistent with previous studies of Ni(II) in chloride-rich ionic media with large organic cations, the $NiCl_4^{2-}$ complex ion forms as the major species in the basic $AlCl_3$–1-BPC room-temperature solvent with apparently little distortion from tetrahedral symmetry.[8] This may be rationalized by arguments similar to those advanced by Øye and Gruen[17] for $CoCl_4^{2-}$ species formation, whereby the dipositive 3d ions are able to combine with free chloride ions and the large electrostatic repulsion energies favor the four- over the six-coordination state. A drastic difference is encountered in the acidic region, and the solvent Al(III) ions, present almost exclusively as $Al_2Cl_7^-$ and $AlCl_4^-$,[1] can only exert weak, if any, influence on the Ni(II) ion core. The nature of such interactions is far less clear; nevertheless, the equilibrium constants obtained from the simple model represented by eq 2 lead to values which are consistent with estimations of the equilibrium constants for the chloroaluminate species, using an aluminum indicator electrode.[1]

Experimental Section

Anhydrous $NiCl_2$ was obtained by sublimation separation from NH_4Cl;[18] and the preparation of materials and melts have been described in earlier papers from this laboratory.[1] Because of the low volatility of these melts at working temperatures, even in the acidic composition range, a simple electrochemical cell may be used. The aluminum reference electrode was a coil of wire (Alfa, m5N) separated from the main cell compartment by a fine-porosity frit and immersed in a 2:1 molar ratio $AlCl_3$–1-BPC melt. For potentiometric measurements a nickel wire (Alfa, m3N7) was cleaned with a H_2SO_4/H_3PO_4/HNO_3 mixture, washed, and dried at room temperature. All experiments were made under purified argon in a Vacuum Atmospheres drybox. Absorption spectra were recorded in 1-cm path length quartz cells, filled and sealed in the drybox, by using a Cary 17 spectrophotometer vs. a blank reference of the appropriate solvent. The densities of the 0.8:1 and 1.5:1 $AlCl_3$–1-BPC melts were taken to be 1.231 and 1.270 g mL^{-1} at room temperature, respectively.

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Registry No. $NiCl_2$, 7718-54-9; $AlCl_3$, 7446-70-0; $NiCl_4^{2-}$, 15320-56-6; 1-butylpyridinium chloride, 1124-64-7.

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