accord with equivalent than with nonequivalent ligands. The complete crystal structure analysis for UL_4 is reported[8] to be in progress.

Pmr spectra for ThL_4 and UL_4 compounds demonstrate the spectroscopic equivalence of all of the C_2H_5 groups in solutions of these chelates. In view of the isolation of the C_2H_5 groups from the metal–sulfur bonds, it is doubtful that the pmr spectra would indicate nonequivalence of the ligands.

The ML_4 compounds react with oxygen and water. ThL_4 can be stored in an inert atmosphere without decomposition, but UL_4, NpL_4, and PuL_4 decompose slowly to form products insoluble in benzene or chloroform. ThL_4 solutions in $CHCl_3$ are stable for days in the absence of oxygen, but decomposition products precipitate from UL_4 solutions within 1 day. The greater stability of ThL_4 is also displayed by the greater ease in preparing a pure compound, compared to the other three ML_4 compounds. Measurements of the Mössbauer spectra of NpL_4 are in progress with the hope of establishing further proof of the structure.

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Distribution of Some Simple and Complex Anions between Molten Lithium Nitrate–Potassium Nitrate and Tetraheptylammonium Nitrate in Polyphenyl

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The distribution of chloride, perrhenate, and $AgCl_2^-$ ions between a eutectic molten salt mixture of $LiNO_3$–KNO_3 and a solution of tetraheptylammonium nitrate in a polyphenyl solvent was studied at 150°. The distribution of the anions has been interpreted in terms of a simple anion-exchange equilibrium followed by polymerization of some species in the organic phase. The equilibrium constants for the anion exchange and the dimerization constants were calculated, and the dependence of the perrhenate distribution on the temperature was determined. The stability constants of AgCl and $AgCl_2^-$ species in the nitrate melt were derived from the distribution data. The activity coefficients of the solute and nitrate salts follow, up to a solute mole fraction of 0.1, an expression derived from a simple model of molten salt mixtures.

Introduction

In contrast to the large number of papers dealing with solvent extraction from aqueous solutions, only few attempts have been made to extend solvent extraction studies to molten salt systems. Isaac, *et al.*,[2a] have studied the extraction of some lanthanides and actinides from molten nitrate with tributyl phosphate, and Hertzog,[2b] in a similar system, extended the study to several other elements. Zangen and Marcus[3] investigated the distribution of mercury(II) halides between a nitrate melt and a polyphenyl solvent while Borkowska, *et al.*,[4] published data on the extraction of some actinides from a KCl–CuCl eutectic melt with various solvents.

The solvent extraction of the anionic species Cl^-, ReO_4^-, and $AgCl_2^-$ from a eutectic $LiNO_3$–KNO_3 melt with tetraheptylammonium nitrate, THAN, in an inert polyphenyl solvent is reported in this paper.

The only solvent extraction studies of metallic complexes involving a molten phase that have been reported are based on the distribution of a neutral species.[2a,3] The stability of metallic complexes in molten nitrates has been studied mainly through electromotive force measurements,[5,6] and owing to the nature of this experimental technique, the information obtained is most reliable for the lower complexes, since the concentration of the ligand is usually low. Thus the formation constant of $AgCl_2^-$ in molten $LiNO_3$–HNO_3[6] seems to be questionable. Solvent extraction and solubility measurements allow the coverage of a wide range of ligand concentration, and with these two independent experimental methods the stability constants of the higher complexes can be determined.

The interpretation of the distribution data in terms of equilibrium constants requires some assumptions regarding the activity coefficients of the species in both phases.

The Melt.—As in all experiments the Li : K mole ratio was maintained constant, the nitrate melt can be taken as a single component M^+A^-, with $M^+ = 0.42Li^+ +$

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[2] (a) N. M. Isaac, P. R. Fields, and D. M. Gruen, *J. Inorg. Nucl. Chem.*, **21**, 152 (1961); (b) D. Hertzog, French Atomic Energy Commission Report R-2628, Dec 1964.

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$0.58K^+$ and $A^- = NO_3^-$. When a salt M^+B^- is added to the nitrate melt, the solution is treated as a binary solution of fused salts with a common cation M^+. For such a system the random mixing of anions in a lattice-like model will be assumed valid. In that case, the excess free energy[7] equals

$$\Delta G^E = (n_A + n_B)x_A x_B \lambda_{AB} \tag{1}$$

where n_A and n_B are the number of moles of M^+A^- and M^+B^-, and x_A and x_B are the mole fractions. The constant λ_{AB} contains the difference between the interaction energy terms of anions A–B and A–A, B–B. It is assumed that for low concentrations of the solute M^+B^-, the B^- anions replace A^- in the "lattice sites" without changing the original structure of the melt.

Differentiation of $\Delta G^E/RT$ with respect to n_B (or n_A) gives the activity coefficients of the components as simple functions of concentration

$$\begin{aligned} \log \gamma_A &= b_{AB}(1 - x_A)^2 \\ \log \gamma_B &= b_{AB}(1 - x_B)^2 \end{aligned} \tag{2}$$

Here, $b_{AB} = \lambda_{AB}/2.303RT$. In these equations the standard state chosen for each component is the pure liquid compound, therefore $\gamma_B = 1$ when $x_B = 1$ and $\gamma_A = 1$ when $x_A = 1$. A reference state defined by $\gamma_B^* = 1$ when $x_B \rightarrow 0$ will be used for the solute. The following relation is valid between the activity coefficients of M^+B^- for these two states

$$\begin{aligned} \mu^\circ_B - \mu^*_B &= RT \ln (\gamma_B/\gamma^*_B) \\ \gamma^\circ_B &= \gamma_B \exp(-\lambda_{AB}/RT) \end{aligned} \tag{3}$$

where μ°_B and μ^*_B are the chemical potentials of M^+B^- in the standard state and reference state, respectively.

For a ternary mixture of salts M^+A^-, M^+B^-, and M^+C^- with a common cation M^+, assuming the same model, eq 1 has the form[7]

$$\Delta G^E = (n_A + n_B + n_C)x_A x_B \lambda_{AB} + x_A x_C \lambda_{AC} + x_B x_C \lambda_{BC}$$

As in the case of a binary mixture, differentiation of $\Delta G^E/RT$ with respect to the mole fraction of a component gives the logarithm of the activity coefficient of that component. If one of the components is present in tracer amounts, all expressions for the activity coefficients are considerably simplified. This is the case in the present study when the concentration of silver is negligible compared to the nitrate and chloride salts. If the components are MNO_3, MCl, and $MAgCl_2$, expressions for the activity coefficients can be derived[7]

$$RT \ln \gamma_{MNO_3} = \lambda_{MNO_3-MCl} x_{MCl}^2 \tag{4}$$

$$RT \ln \gamma^*_{MCl} = \lambda_{MNO_3-MCl}(x_{MCl}^2 - 2x_{MCl}) \tag{5}$$

$$RT \ln \gamma^*_{MAgCl_2} = (\lambda_{MCl-MAgCl_2} - \lambda_{MNO_3-MAgCl_2} - \lambda_{MNO_3-MCl})x_{MCl} + \lambda_{MNO_3-MCl} x_{MCl}^2 \tag{6}$$

Here again, γ^* refers to the reference state ($\gamma^* = 1$ when $x \rightarrow 0$). In the case that $AgCl_2^-$ dissociates into AgCl and Ag^+ at low chloride concentration, it is assumed that eq 6 is still valid, but $\gamma^*_{MAgCl_2}$ is then close to unity. In that case the activity coefficients of all other silver species are assumed equal to unity, and according to Bjerrum,[8] the "degree of formation" of $AgCl_2^-$ can be defined as

$$\alpha_2 = \frac{[AgCl_2^-]}{[Ag^+] + [AgCl] + [AgCl_2^-]} = \frac{[AgCl_2^-]}{c_{Ag}} \tag{7}$$

The Organic Solvent.—It is assumed that the tetraheptylammonium salt in the polyphenyl solvent is in the form of undissociated ion pairs. Solvent–solvent and solvent–solute interactions are neglected, and only solute–solute interactions are considered. These interactions could be treated, in principle, by activity coefficients, but it is believed that a better approach is to assume that all activity coefficients of organic species are equal to unity and handle the solute–solute interactions in the organic solvent by ion-pair aggregation. This approach is supported by recent osmometric measurements of tetraheptylammonium chloride in benzene at 25°, which could be explained in terms of "polymerization" of the quaternary salt.[9]

If $\overline{TNO_3}$ is the tetraheptylammonium nitrate ion pair and $\overline{TX}$ a similar ion pair with anion X^- instead of NO_3^-, then three types of polymers can be formed in the organic phase: homopolymers $\overline{(TNO_3)_m}$ and $\overline{(TX)_n}$ and heteropolymers $\overline{(TNO_3)_m(TX)_n}$. The polymerization constants are defined by the general expression

$$k_{mn} = \frac{[\overline{T(NO_3)_m(TX)_n}]}{[\overline{TNO_3}]^m[\overline{TX}]^n} \tag{8}$$

where the bar refers to the species in the organic phase. If X^- is in tracer amount, the formation of $\overline{(TX)_n}$ homopolymers can be neglected.

The Distribution Equilibrium.—The over-all extraction equilibrium between a solute M^+X^+ in the melt and $\overline{TNO_3}$ in the organic solvent can be described by equations of the type

$$nM^+X^- + (m + n)\overline{TNO_3} = \overline{(TX)_n(TNO_3)_m} + nM^+NO_3^-$$

Whatever the values of n and m, these equations can be expressed by one heterogeneous equilibrium which is a simple anion exchange

$$M^+X^- + \overline{TNO_3} = \overline{TX} + M^+NO_3^-$$

and by polymer formation in the organic solvent

$$m\overline{TNO_3} + n\overline{TX} = \overline{(TNO_3)_m(TX)_n}$$

The equilibrium constant for the ion-exchange reaction is

$$\begin{aligned} K_d &= \frac{[\overline{TX}][M^+NO_3^-]}{[\overline{TNO_3}][M^+X^-]} \frac{\gamma_{MNO_3}}{\gamma^*_{MX}} \\ K_d &= K_d^c \gamma_{MNO_3}/\gamma^*_{MX} \end{aligned} \tag{9}$$

K_d^c is the concentration quotient which becomes K_d as the concentration of M^+X^- approaches zero. The equilibrium constant for the formation of the polymer is given by eq 8.

The distribution ratio of the anion X^- between the solvent and the melt is defined as the ratio between the

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concentration of total X in the organic solvent and the melt

$$D = \frac{\overline{m}_X}{m_X}$$

Here, $\overline{m}_X$ is moles of X^-/1000 g of polyphenyl solvent, and m_X is moles of X^-/1000 g of $(Li,K)NO_3$ melt.

Let us assume that at low X^- concentration in the melt a certain range of THAN concentration exists so that practically only four species are present in the organic solvent: $\overline{TNO_3}$, $\overline{TX}$, $\overline{(TNO_3)_2}$, and $\overline{TNO_3 \cdot TX}$. In that case, according to eq 8, two dimerization constants can be defined

$$k_{20} = \frac{[\overline{(TNO_3)_2}]}{[\overline{TNO_3}]^2} \qquad (10)$$

$$k_{11} = \frac{[\overline{TNO_3 \cdot TX}]}{[\overline{TNO_3}][\overline{TX}]} \qquad (11)$$

The total concentration of THAN in the organic solvent not bound to X^- equals then

$$c_T = [\overline{TNO_3}] + 2[\overline{(TNO_3)_2}] = [\overline{TNO_3}] + 2k_{20}[\overline{TNO_3}]^2 \quad (12)$$

and the distribution ratio

$$D = \frac{[\overline{TX}] + [\overline{TNO_3 \cdot TX}]}{[MX]}$$

$$D = \frac{K_d^c}{[M^+NO_3^-]}[\overline{TNO_3}] + \frac{K_d^c k_{11}}{[M^+NO_3^-]}[\overline{TNO_3}]^2 \qquad (13)$$

At low concentration of X^-, $\gamma_{MNO_3}/\gamma^*_{MX} = 1$ and $K_d^c = K_d$. In this particular case, K_d and k_{11} can be obtained by means of eq 13, by plotting $D/[\overline{TNO_3}]$ *vs.* $[\overline{TNO_3}]$ if the equilibrium concentration of the monomer $[\overline{TNO_3}]$ is known. If $[\overline{TNO_3}]$ is not known, a method of successive approximation can be used to obtain K_d, k_{11}, and k_{20}. A family of curves of $D/[\overline{TNO_3}]$ *vs.* $[\overline{TNO_3}]$ is plotted, assuming different values of k_{20} to calculate $[\overline{TNO_3}]$, until a straight line is obtained. The best value of k_{20} can be chosen by taking into account the distribution of various solute anions since this constant should not depend on the nature of the extracted species.

This method of evaluating the equilibrium constants is applicable to systems in which only monomers and dimers are the principal species in the organic solvent over a concentration range of two to three orders of magnitude.

Experimental Section

The Organic Solution.—Tetraheptylammonium nitrate (THAN) was chosen after a qualitative screening of some quaternary salts for thermal stability, solubility in the polyphenyl solvent, and ease of preparation. The nitrate salt was prepared from tetraheptylammonium iodide (Eastman White Label) which was dissolved in benzene, and the solution was shaken with an aqueous solution of $AgNO_3 + HNO_3$. The organic phase was separated from the aqueous solution and precipitate, filtered, then washed with 0.1 *M* HNO_3 and water. Neither Ag^+ nor I^- could be detected in the last wash solutions. The benzene solution of THAN was concentrated by evaporation on a steam bath, petroleum ether (bp 30–60°) was added, the solution was cooled to about 4°, and the THAN was removed by filtration. The salt, recrystallized twice from a benzene–petroleum ether solvent and dried 48 hr under vacuum, had a melting point of 103–104° (uncor). An assay of 99.2 ± 0.5% was obtained by passing a methanol–water solution of the salt through a Dowex 50-8X cation-exchange column in acid form and titrating the liberated HNO_3. *Anal.* Calcd for $C_{28}H_{60}N_2O_3$: C, 71.13; H, 12.39; N, 5.93. Found: C, 71.38; H, 12.72; N, 6.20. Samples of THAN heated in air for 1 hr at 150° lost weight and assay of 0.6 ± 0.5%.

The organic solvent was the eutectic mixture of *o*-terphenyl, *m*-terphenyl, and biphenyl. Its composition in mole fractions was 0.48, 0.15, and 0.37, respectively, and its melting point 23°.[10] The solvent, prepared from Eastman White Label chemicals, was passed through a layer of Alcoa activated alumina (Grade F-20, 80–200 mesh) which absorbed traces of slightly colored impurities and also served as a drying agent.

The Melt.—The melt was the eutectic mixture of $LiNO_3$–KNO_3, 0.42 mole fraction of $LiNO_3$, with a melting point of 123°.[11–13] It had 11.42 moles of nitrate/1000 g of melt. The mixture was prepared from reagent grade salts which were dried at 150° for several days. After fusion, the melt was filtered through Pyrex glass wool, and then the last traces of water were removed by bubbling dry nitrogen through it at 240–250° for 4–5 hr.

Radioactive Tracers.—The ^{186}Re tracer was obtained by irradiating 1–2 mg of rhenium metal in the MIT reactor. After a cooling time of 48 hr, the metal was dissolved in a mixture of $H_2O_2 + NH_3$ and the solution evaporated to dryness. The dry NH_4ReO_4 residue was dissolved in the melt.

The ^{38}Cl and tracer was obtained by irradiation of 1–2 mg of NH_4Cl salt in the reactor. The ^{110m}Ag tracer was obtained from the New England Nuclear Corp.

In some experiments inactive isotopic carriers were added to the melt, *i.e.*, KCl and $KReO_4$. In experiments in which higher concentrations of these salts were needed, a mixture of lithium and potassium salts was added to maintain the same mole ratio of Li:K as in the eutectic nitrate melt.

Experimental Technique.—A weighed amount of melt, usually 5–6 g, was equilibrated with approximately equal weight of solvent in 10-ml Pyrex centrifuge tubes with Teflon stoppers. The equilibration was carried out in a forced-air-circulating thermostated oven (Fisher's Isotemp) at 150 ± 1° (except for a few experiments at other specified temperatures). Through the door of the oven a rotating shaft, driven externally by a small electric motor, was installed, with a facility to fix six tubes at a convenient angle. By rotating the assembly of tubes at 60 rpm, a good mixing of phases in the tubes was achieved. Aliquots were taken from both phases into vials, with preheated disposable glass pipets. The melt and solvent aliquots were weighed, dissolved in water and in benzene, respectively, and then counted in a well-type γ-scintillation counter.

The molal distribution ratio, *D*, was calculated as the ratio between the counting rate per gram of polyphenyl solvent and the counting rate per gram of nitrate melt. Every distribution coefficient is the average value of two to five independent experiments. The standard deviation of the distribution coefficients is 1–5%, except in the range of *D* of 10^{-3} or below, where it is up to 10%. Concentrations are expressed in molality, except in a few cases when the use of mole fraction was more convenient.

Results and Discussion

The Distribution of ReO_4^- and Cl^-.—Preliminary experiments have shown that by mixing the two phases equilibrium is reached after 30–60 min. In all distribution experiments an equilibration time of 60 min was chosen.

The extraction data for ReO_4^- and Cl^- are summarized in Tables I and II as *D vs.* initial THAN con-

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Table I

ReO_4^- Distribution at 150°

c_T^i, *m*	*D* ($[\overline{ReO_4}]/[ReO_4]$)	c_X^i, *m*
1.00×10^{-1}	3.14	
8.00×10^{-2}	2.80	
5.00×10^{-2}	1.69	
2.98×10^{-2}	8.31×10^{-1}	
2.00×10^{-2}	6.01×10^{-1}	
1.50×10^{-2}	4.73×10^{-1}	
1.00×10^{-2}	3.12×10^{-1}	$\sim 1 \times 10^{-5}$
8.00×10^{-3}	2.49×10^{-1}	
5.00×10^{-3}	1.59×10^{-1}	
3.40×10^{-3}	1.08×10^{-1}	
2.00×10^{-3}	6.85×10^{-2}	
1.13×10^{-3}	4.10×10^{-2}	
3.30×10^{-4}	1.25×10^{-2}	
1.00×10^{-1}	2.93	
3.00×10^{-2}	9.39×10^{-1}	
1.00×10^{-2}	2.86×10^{-1}	1.00×10^{-3}
3.00×10^{-3}	9.57×10^{-2}	
1.00×10^{-3}	3.43×10^{-2}	
2.00×10^{-2}	5.73×10^{-1}	5.00×10^{-3}
4.02×10^{-3}	1.22×10^{-1}	
1.00×10^{-1}	2.39	
3.00×10^{-2}	7.10×10^{-1}	
1.00×10^{-2}	2.55×10^{-1}	1.00×10^{-2}
3.00×10^{-3}	7.86×10^{-2}	
1.00×10^{-3}	2.88×10^{-2}	
	2.86×10^{-1}	1.00×10^{-3}
	2.66×10^{-1}	9.90×10^{-3}
	2.17×10^{-1}	2.01×10^{-2}
	1.61×10^{-1}	4.00×10^{-2}
1.00×10^{-2}	1.48×10^{-1}	4.80×10^{-2}
	1.25×10^{-1}	5.97×10^{-2}
	1.03×10^{-1}	7.92×10^{-2}
	9.20×10^{-2}	9.07×10^{-2}
	7.69×10^{-2}	1.16×10^{-1}

Table II

Chloride Distribution at 150°

c_T^i, *m*	*D* ($[\overline{Cl}]/[Cl]$)	c_X^i, *m*
1.00×10^{-1}	4.82×10^{-3}	
6.00×10^{-2}	3.66×10^{-3}	
4.00×10^{-2}	2.88×10^{-3}	
2.00×10^{-2}	1.82×10^{-3}	
1.00×10^{-2}	1.19×10^{-3}	7.93×10^{-2}
1.00×10^{-2}	1.19×10^{-3}	
5.00×10^{-3}	7.4×10^{-4}	
2.00×10^{-3}	4.0×10^{-4}	
1.00×10^{-3}	2.2×10^{-4}	
1.00×10^{-1}	4.96×10^{-3}	
3.00×10^{-2}	2.21×10^{-3}	
1.00×10^{-2}	1.05×10^{-3}	1.01×10^{-1}
3.00×10^{-3}	5.1×10^{-3}	
1.00×10^{-3}	1.6×10^{-4}	
1.00×10^{-1}	3.58×10^{-3}	
3.00×10^{-2}	1.58×10^{-3}	
1.00×10^{-2}	7.3×10^{-4}	1.00
3.00×10^{-3}	2.0×10^{-4}	
1.00×10^{-3}	1.1×10^{-4}	
	1.09×10^{-3}	5.97×10^{-2}
	1.04×10^{-3}	1.01×10^{-1}
	1.01×10^{-3}	1.07×10^{-1}
	9.7×10^{-4}	2.02×10^{-1}
1.00×10^{-2}	9.8×10^{-4}	2.97×10^{-1}
	9.7×10^{-4}	3.96×10^{-1}
	9.2×10^{-4}	5.86×10^{-1}
	8.2×10^{-4}	7.06×10^{-1}
	8.6×10^{-4}	8.70×10^{-1}
	7.3×10^{-4}	1.00

centration c_T^i and initial M^+X^- concentration c_X^i in the melt ($X^- = ReO_4^-$, Cl^-).

An analysis of the data indicates that below a THAN concentration of about 10^{-3} *m* the distribution of X^- follows the simple anion exchange

$$X^- + \overline{TNO_3} = \overline{TX} + NO_3^-$$

However, the formation of polymeric species in the organic phases cannot be neglected at higher concentrations of THAN.

It is possible to explain the ReO_4^- extraction at low initial concentration of ReO_4^- in the melt by assuming four species in the organic phase, $\overline{TReO_4}$, $\overline{TReO_4 \cdot TNO_3}$, $\overline{TNO_3}$, and $\overline{(TNO_3)_2}$. The equilibrium constants for the extraction of ReO_4^- were obtained by using the method described earlier. The chloride extraction data were analyzed in the same way and a final value of k_{20} chosen so that the best fit was obtained for the distribution of both anions. The K_d and k_{11} values were obtained by means of eq 13 using the least-square method. The equilibrium constants are reported in Table III. The distribution coefficients of chloride are much lower than those of perrhenate and somewhat less precise. However, by means of the dimerization constant k_{20} for THAN, the distribution of chloride can be explained also by eq 13 with $k_{11} = 0$, *i.e.*, assuming only $\overline{TCl}$ as the chloride species in the organic solvent.

Table III

Equilibrium Constants at 150° (Molality Scale)

Symbol	Eq	Equil	Equil constant
K_d	9	ReO_4^-–NO_3^-	420 ± 20
	9	Cl^-–NO_3^-	2.1 ± 0.2
	15	$AgCl_2$–NO_3^-	2510 ± 20
k_{20}	10	Dim. $\overline{(TNO_3)_2}$	50 ± 5
k_{11}	11	Dim. $\overline{TNO_3 \cdot TReO_4}$	59 ± 12
K_1	19	AgCl formation	310 ± 20
K_2	20	$AgCl_2^-$ formation	125 ± 10

The equilibrium constants K_d in Table III refer to the reference state defined by $\gamma^*_{MX} = 1$ and $\gamma_{MNO_3} = 1$ when $x_{MX} \rightarrow 0$. Figure 1 shows how the calculated constants fit the distribution of ReO_4^- and Cl^-. The points are experimental values of *D* and the curves represent the dependence of *D* on the concentration of the $\overline{TNO_3}$ monomer in the solvent, calculated from eq 13 and with the values of constants from Table III. The concentration of the monomer $\overline{TNO_3}$ was calculated from the total concentration of THAN using eq 10 and 12. The two lowest experimental *D* values for Cl^- are not in good agreement with the calculated curve. However, the absolute values are so small that the discrepancies could be explained if the pure diluent extracts chloride with $D \approx 10^{-5}$. In the case of ReO_4^-, deviations at high concentration of THAN are probably due to the effect of higher polymers, which are neglected in the present treatment.

The dependence of the distribution coefficient *D* on the solute anion (X^-) concentration in the melt (the last set of data in Tables I and II) can furnish

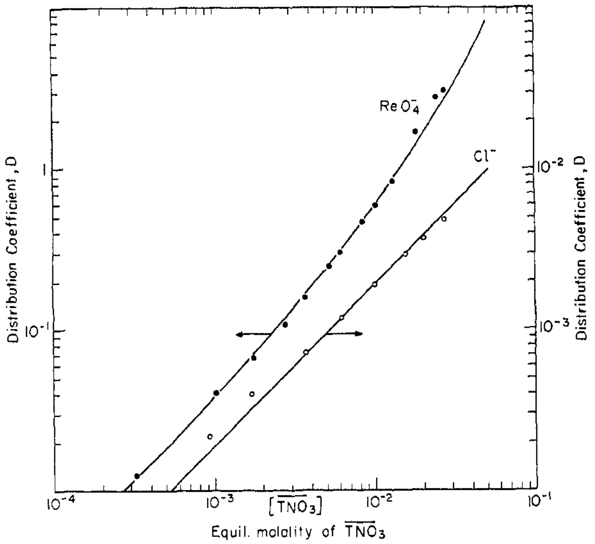

Figure 1.—The distribution of ReO_4^- and Cl^- (150°). D vs $[\overline{TNO_3}]$. Initial ReO_4^- concentration 1.0×10^{-5} *m;* initial Cl^- concentration 7.93×10^{-2} *m.*

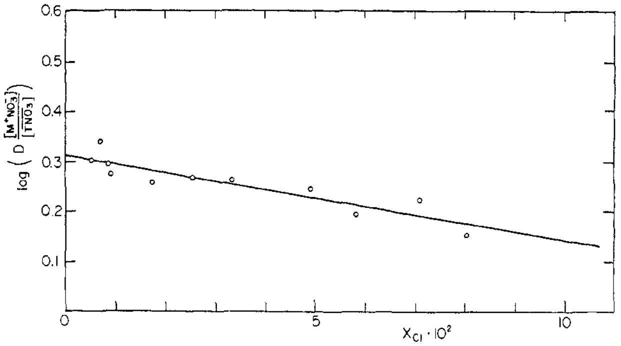

Figure 2.—The dependence of Cl^- distribution on the mole fraction of chloride in the melt (eq 14). Constant THAN concentration in the solvent 10^{-2} *m.*

some additional information on the species in the organic solvent. For perrhenate the data indicate that $(\overline{TReO_4})_2$ and probably also higher polymers are formed.

In the case of chloride (last set of data in Table II) the behavior is different. The distribution of chloride is about two orders of magnitude lower than that of perrhenate anion, so that at 1 *m* chloride concentration in the melt, only about 7% of THAN is in the chloride form. As shown in Figure 2, in the case of Cl^- extraction D is directly proportional to the $\overline{TNO_3}$ concentration. Thus the polymeric species $\overline{TCl \cdot TNO_3}$ and $(\overline{TCl})_2$ are not important in the organic phase, and it seems reasonable to assume that up to 1 *m* chloride concentration in the melt $\overline{TCl}$ is still the principal chloride species in the organic solvent. Thus, the decrease of D with increasing chloride concentration in the melt can be attributed to changes in the activity coefficients of the nitrate and chloride components of the melt. If eq 9 and 13 are combined and the term with k_{11} is neglected, the following expression should be valid

$$\log D\frac{[M^+NO_3^-]}{[\overline{TNO_3}]} = \log K_d + \log \frac{\gamma^*_{MCl}}{\gamma_{MNO_3}}$$

If the activity coefficients are expressed by means of eq 2 and 3, the dependence of D on the chloride concentration in the melt should follow the simple relation

$$\log D\frac{[M^+NO_3^-]}{[\overline{TNO_3}]} = \log K_d - 2b_{AB}x_{Cl} \qquad (14)$$

Here, x_{Cl} is the mole fraction of chloride in the melt. The concentration of the monomeric $\overline{TNO_3}$ can be calculated by subtracting from $c_T{}^i$ the concentration of chloride in the organic solvent and then using eq 10 and 12.

Equation 14 is compared with the experimental data in Figure 2. Errors in determining low values of D cause a considerable scattering in the experimental points, so that K_d and b_{AB} cannot be calculated with high precision. It was found that $b_{AB} = 0.85$ which corresponds to $\lambda_{AB} = 1.65$ kcal. The equilibrium constant K_d is 0.43 ± 0.04 if the pure liquid component is taken as the standard state, or 2.1 ± 0.2 as given in Table III if it refers to the dilute solution as reference state, defined by $\gamma^*_{Cl} = 1$ for $x_{Cl} \rightarrow 0$.

With the present systems, the possibility of varying the temperature is rather restricted. At one side the limit is set by the freezing point of the melt, while on the other side the limiting factor is the thermal stability of THAN. Therefore only experiments within the range 140–160° were carried out. In the case of chloride the low D values were not precise enough to draw any conclusions, while in the case of perrhenate a distinct temperature dependence of D is found, as shown in Table IV. The K_d's in this table were obtained by extrapolating to $c_T{}^i = 0$ the plots of log $\{D[M^+NO_3]/c_T{}^i\}$ *vs.* $c_T{}^i$. (For $c_T{}^i < 10^{-2}$, the extrapolation is practically linear.) The standard enthalpy change for the simple anion-exchange reaction was found to be $\Delta H°_{423} = -11.7$ kcal mol^{-1}, from the slope of the curve of log K_d *vs.* $1/T$.

The Distribution of $AgCl_2^-$.—The distribution ratio of silver to chloride between a melt approximately 0.5 *m* in MCl and 10^{-3} *m* in $AgNO_3$ and an organic phase 10^{-2} *m* in TNO_3 was determined using 260-day ^{110m}Ag and 37-min ^{38}Cl as tracers in two samples of this melt. The results are shown in Table V. These data confirm the assumption that the ratio of Cl to Ag in the extracted species is 2:1.

On the basis of this result the distribution of silver can be described by the ion-exchange equilibrium

$$M^+AgCl_2^- + \overline{TNO_3} = \overline{TAgCl_2} + M^+NO_3^-$$

$$K_d = \frac{[\overline{TAgCl_2}][M^+NO_3^-]\gamma_{MNO_3}}{[\overline{TNO_3}][M^+AgCl_2^-]\gamma^*_{MAgCl_2}} \qquad (15)$$

The distribution ratios of silver nitrate species are about two orders of magnitude lower than those of chloride species. Hence, if $\overline{TAgCl_2}$ is the only silver species in the organic phase, then

$$D = [\overline{TAgCl_2}]/c_{Ag} \qquad (16)$$

Here c_{Ag} is, as in eq 7, the total concentration of silver in the melt.

Table IV

The Dependence of ReO_4^- Extraction on Temperature[a]

140°		150°		160°	
c_T^i	D	c_T^i	D	c_T^i	D
2.97×10^{-4}	1.50×10^{-2}	3.30×10^{-4}	1.25×10^{-2}	2.97×10^{-4}	7.79×10^{-3}
9.88×10^{-4}	4.25×10^{-2}	1.13×10^{-3}	4.10×10^{-2}	9.88×10^{-4}	2.57×10^{-2}
2.97×10^{-3}	1.09×10^{-1}	2.00×10^{-3}	6.85×10^{-2}	2.97×10^{-3}	7.20×10^{-2}
3.01×10^{-2}	1.11	3.40×10^{-3}	1.08×10^{-1}	1.00×10^{-2}	2.35×10^{-1}
$K_d = 580 \pm 60$		$K_d = 420 \pm 20$		$K_d = 300 \pm 10$	

[a] Initial ReO_4 concentration in the melt 10^{-5} m.

Table V

The Ratio of Chloride to Silver in the Organic Phase

Initial molality in melt		Distribution ratio		Equil molality in organic phase		Molality of Cl bound to Ag in organic phase	Mole ratio Cl/Ag =
m_{Cl}^i	m_{Ag}^i	D_{Cl}	D_{Ag}	m_{Cl}	m_{Ag}	m'_{Cl}	m'_{Cl}/m_{Ag}
0.500	9.75×10^{-4}	2.78×10^{-3}	7.90×10^{-1}	1.39×10^{-3}	4.60×10^{-4}	9.30×10^{-4}	2.02
0.500	9.91×10^{-4}	2.92×10^{-3}	8.03×10^{-1}	1.46×10^{-3}	4.65×10^{-4}	1.00×10^{-3}	2.15
0.500	...	9.20×10^{-4}	...	4.60×10^{-4}	...	...	...

Introducing eq 7 and 16 into eq 15, eq 17 is obtained

$$\log D = \log K_d + \log [\overline{TNO_3}] + \log \frac{\alpha_2 \gamma^*_{MAgCl_2}}{[M^+NO_3^-]\gamma_{MNO_3}} \quad (17)$$

The distribution ratio D of silver at tracer concentrations was measured at 150 ± 1° as a function of $\overline{TNO_3}$ concentration for a melt 0.2 m in MCl. Under the conditions of the experiments, constant concentration of MCl and tracer amounts of silver, the last term of eq 17 is constant. A plot of log D *vs.* log $[\overline{TNO_3}]$ is shown in Figure 3, and as expected the slope is +1 over two powers of 10 in $\overline{TNO_3}$. The concentration of monomer $\overline{TNO_3}$ was calculated from eq 10 and 12 with $k_{20} = 50$ from Table III.

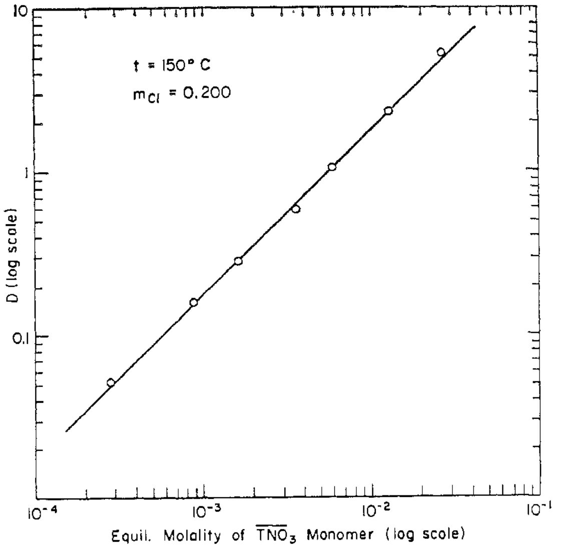

Figure 3.—Dependence of the distribution ratio of Ag(I)–Cl complexes on $\overline{TNO_3}$ concentration.

The dependence of D on the concentration of MCl was also studied and the results are shown in Figure 4. For the interpretation of these results, the following relation can be obtained from eq 4, 6, and 17

$$\log (D[M^+NO_3^-]/[\overline{TNO_3}]) = \log K_d + \log \alpha_2 + b_{ABC}x_{Cl} \quad (18)$$

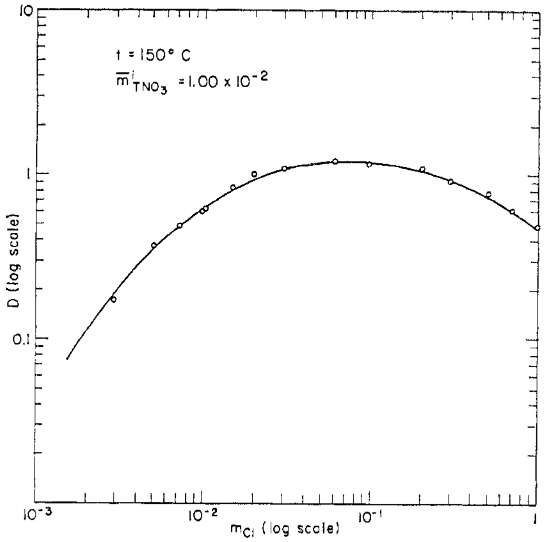

Figure 4.—Dependence of the distribution ratio of Ag(I)–Cl complexes on chloride concentration.

where $b_{ABC} = (\lambda_{MCl-MAgCl_2} - \lambda_{MNO_3-MAgCl_2} - \lambda_{MNO_3-MCl})/2.303RT$, and x_{Cl} is the mole fraction of the chloride in the melt. The plot of log $(D[M^+NO_3^-]/[TNO_3])$ *vs.* x_{Cl} is shown in Figure 5. The linear portion of the graph is the result of $\alpha_2 = 1$. The line was established by a least-square analysis. At lower concentrations of MCl, α_2 decreases and the species AgCl and Ag^+ become important. The slope of the line is b_{ABC}, with a value of −5.48. The ordinate intercept of the line gives K_d with a value of 2510 ± 20. From these values α_2 was calculated and its dependence on x_{Cl} is also shown in Figure 5.

The activity coefficients of the anionic species can be calculated from eq 4–6 and the above value of b_{ABC} and the value of $b_{AB} = 0.85$ obtained previously. For x_{Cl} below 2×10^{-3} the calculated activity coefficients are within 2% of unity, and since this is within the experimental error in D, the activity coefficients are considered equal to unity in this range of concentrations. The activity coefficients given by eq 4–6

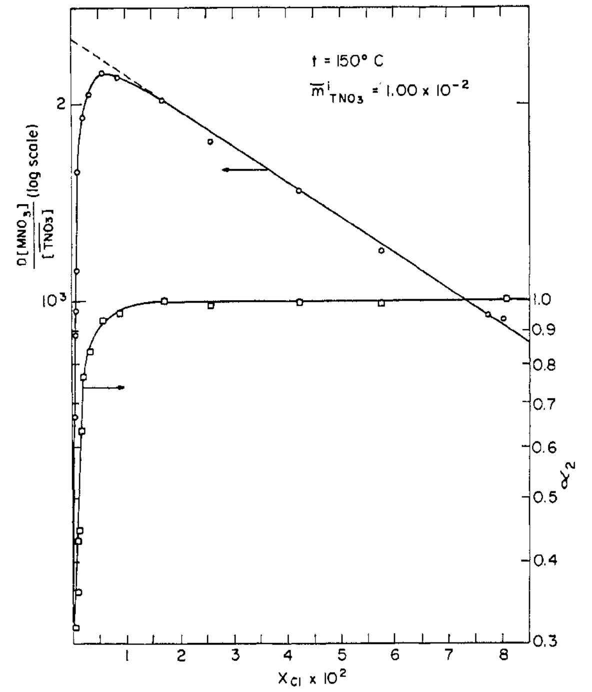

Figure 5.—Dependence of $D[MNO_3]/[\overline{TNO_3}]$ and α_2 on chloride mole fraction.

correspond to the mole fraction scale and they are related to the molality scale through the relation

$$\gamma(\text{molality}) = \gamma(\text{mole fraction})x_{NO_3}$$

The stability constants K_1 and K_2 defined by

$$Ag^+ + Cl^- = AgCl$$

$$K_1 = [AgCl]/[Ag^+][Cl^-]\gamma^*_{Cl} \qquad (19)$$

and

$$AgCl + Cl^- = AgCl_2^-$$

$$K_2 = [AgCl_2^-]\gamma^*_{AgCl_2}/[AgCl][Cl^-]\gamma^*_{Cl} \qquad (20)$$

were calculated from α_2 using the curve-fitting methods described by Rossotti and Rossotti.[14] The values obtained are given in Table III.

Values of K_1 and K_2 have been determined by electromotive force measurements[6] and by solubility measurements.[15] These values are in good agreement with those given in Table III, except K_2 obtained by the emf method, which seems to be questionable. The significance of the two equilibrium constants in respect to a quasi-lattice model of molten salt is discussed elsewhere.[15]

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Monocyanochromium(III) Ion: Kinetics of the Spontaneous Aquation and of the Chromium(II)- and Mercury(II)-Catalyzed Reactions[1]

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The kinetics of loss of cyanide ion from the complex $(H_2O)_5CrCN^{2+}$ has been studied as a function of hydrogen ion concentration and temperature in solutions of unit ionic strength, in which the supporting electrolyte was either sodium or lithium perchlorate. Small differences in the two sets of results were found, which were attributed to medium effects arising from a nonconstant activity coefficient of hydrogen ion in solutions of constant ionic strength but varying composition. At 55.0° and $\mu = 1.00\ M$ (lithium perchlorate medium) the aquation rate is given by the equation $-d\ln[CrCN^{2+}]/dt = 5.8 \times 10^{-7}[H^+]^{-1} + 9.7 \times 10^{-4} + 8.0 \times 10^{-3}[H^+]\ sec^{-1}$. The catalysis by chromium(II) is consistent with an expression $k[CrCN^{2+}][Cr^{2+}]/[H^+]$ with $k = 2.8 \pm 0.3 \times 10^{-3}\ sec^{-1}$ at 55.0° and $\mu = 1.00\ M$. Mercury(II) and $CrCN^{2+}$ associate quite strongly; the association quotient of $Cr(CN)Hg^{4+}$ is $\geq 10^5\ M^{-1}$. Aquation in the presence of mercury(II) is described by the relation $d[Cr^{3+}]/dt = k_{Hg}[Cr(CN)Hg^{4+}]$, with $k_{Hg} = 6.6 \pm 0.9 \times 10^{-3}\ sec^{-1}$. The mechanisms of the three reactions are discussed from the standpoint of the net activation processes and the compositions and likely geometries of the transition states involved. Evidence is advanced for the proposal that the reaction of $CrCN^{2+}$ and Hg^{2+} is accompanied by internal ligand isomerization and that the cation complex is $Cr\text{–}NC\text{–}Hg^{4+}$.

Introduction

The pentaaquomonocyanochromium(III) cation, $(H_2O)_5CrCN^{2+}$, has been produced from the reduction of monocyanocobalt(III) complexes by chromium(II) ion in acidic solutions.[2,3] The same complex results from the stepwise decomposition of $Cr(CN)_6^{3-}$ in acidic

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[1] Work performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission; Contribution No. 2232. Based in part on the Ph.D. thesis of J. P. B., Iowa State University, May 1967.

[2] J. H. Espenson and J. P. Birk, *J. Am. Chem. Soc.*, **87**, 3280 (1965).

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