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Redox Potentials in Ammonium Nitrate Solutions

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The redox potentials of M^{n+}/M ($M^{n+} = Cu^{2+}, Pb^{2+}, Sn^{2+}, Cd^{2+}, Ag^{+}, Zn^{2+}, Hg^{2+}$), $M^{n+}/M^{(n-m)+}$ (Fe^{3+}/Fe^{2+}, $Fe(CN)_6 3^-/Fe(CN)_6^{4-}$), and AgX/Ag, X^- (X = Cl, Br, and I) have been measured in aqueous solutions of ammonium nitrate (1–14 M). The variation of solvation of ions, characterized by the solvent transfer coefficient f^{tr}, is calculated from the normal redox potentials of the systems. For all the cases, the potential of the ferricinium/ferrocene system (Fc^+/Fc) is used as a reference of potential. It appears as a general trend that when the concentration of salt increases from 1 to 14 M, the potentials of the systems vary slightly, indicating weak interactions between these solutes and the salt. The examined ions can be classified into two groups: those that are less solvated as the concentration of NH_4NO_3 increases (Cu^{2+}, Cd^{2+}, Zn^{2+}, Cl^-, Br^-, I^-) and those that are more solvated, (Pb^{2+}, Ag^+, Hg^{2+}, Sn^{2+}). The solubility constants of the AgX salts in the $H_2O + NH_4NO_3$ mixtures are also calculated.

Introduction

Concentrated aqueous acid or salt solutions are extensively employed for the recovery of mineral products by liquid–liquid extraction, ion exchange, or ionic flotation (*1–3*). Many works, over the past two decades have been devoted to the study of the physicochemical properties of these media (*4–8*). Their solvation properties must be specified when one is interested in the evolution of the reactivity of ionic species with acid or salt concentration. Information on solvation properties of ionic and molecular species which are characterized by their solvent transfert activity coefficient f^{tr} can be obtained by analyzing electrochemical data (*7*, *8*). Such results allow prediction of the changes in solubility of mineral compounds and the variations of redox properties of metals with the composition of a water + salt mixture. Indeed, the improvement of solvent extraction or ion exchange extraction processes of many species depends upon the knowledge of their solvation properties and their oxidation state. This work seeks to study the variation of the solvation of ions in $H_2O + NH_4NO_3$ (1–14 M) in order to estimate the evolution of the redox properties, the ion reactivity, and the solubility of the components. Our interest in studying the physicochemical properties of highly concentrated aqueous ammonium nitrate solutions is derived from the fact that their solvation properties have not, to our knowledge, been investigated although these media are suitable for electrochemistry, ionic flotation, and liquid–liquid extraction. The redox systems have been chosen for their easy characterization by electrochemical methods and for their economic interest.

Theoretical Aspects

Solvation and Redox Properties. The procedure previously described for phosphoric acid media (*5*), for chloride acid media (*6*), for phosphoric acid + sodium hydroxide mixtures (*7*), and for strong acid mixtures (*9*) has been applied to the case of ammonium nitrate solutions. It is based on the use of the extrathermodynamic assumption of Strehlow (*8*).

Given the following oxidation–reduction reaction

$$A + ne \leftrightarrow B \qquad (1)$$

in a sufficiently diluted solution of A and B in water (close to 10^{-4} M), the potential of the solution involving the couple A/B at 298 K is given by

$$E_{H_2O} = E^\circ_{H_2O} + (0.059/n)\log c_A/c_B \qquad (2)$$

where c_A and c_B are the molar concentrations of the solutes, the normal potential $E^\circ_{H_2O}$ being given compared with the ferricinium/ferrocene system chosen as the reference potential (*8*). In a concentrated aqueous ammonium nitrate solution, relation 2 will still be suitable provided that the activities $a_A = f^{tr}{}_A c_A$ and $a_B = f^{tr}{}_B c_B$ of the species A and B are used, c_A and c_B being the molar concentrations of these species in the NH_4NO_3 solution and $f^{tr}{}_A$ and $f^{tr}{}_B$ being the solvent transfer activity coefficients of species A and B from dilute aqueous solution taken as reference to the concentrated NH_4NO_3 aqueous solutions:

$$E_{H_2O+NH_4NO_3} = E^\circ_{H_2O+NH_4NO_3} + (0.059/n)\log(f^{tr}{}_A/f^{tr}{}_B) + (0.059/n)\log c_A/c_B \qquad (3)$$

The normal potential of ferricinium/ferrocene is always considered as the reference potential in these media. The redox couple A/B is therefore characterized in the $H_2O + NH_4NO_3$ media by the normal potential $E^\circ_{H_2O+NH_4NO_3}$ given by

$$E^\circ_{H_2O+NH_4NO_3} = E^\circ_{H_2O} + (0.059/n)\log f^{tr}{}_A/f^{tr}{}_B \qquad (4)$$

In the particular cases of the following redox reactions where the subscript s is relative to the solid species,

$$M^{n+} + ne^- \leftrightarrow M(s) \qquad (5)$$

$$M^{n+} + me^- \leftrightarrow M^{(n-m)+} \qquad (6)$$

$$AX_p + pe^- \leftrightarrow A(s) + pX^- \qquad (7)$$

eq 4 takes the forms

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$$E^{\circ}_{H_2O+NH_4NO_3} = E^{\circ}_{H_2O} + (0.059/n)\log f^{tr}_{M^{n+}} \qquad (8)$$

$$E^{\circ}_{H_2O+NH_4NO_3} = E^{\circ}_{H_2O} + (0.059/m)\log(f^{tr}_{M^{n+}}/f^{tr}_{M^{(n-m)+}}) \qquad (9)$$

$$E^{\circ}_{H_2O+NH_4NO_3} = E^{\circ}_{H_2O} - 0.059\log f^{tr}_{X^-} \qquad (10)$$

Therefore, the solvent transfer activity coefficients f^{tr} characterize the variation of solute solvation. They are determined from normal potential values of the corresponding redox systems according to relations 8–10.

Solvation and Solubility. Insoluble species of the form MX(s) are capable of partial dissociation into M^+ and X^- ions according to the following equilibrium:

$$MX(s) \leftrightarrow M^+ + X^- \qquad (11)$$

If one assumes that no associated ions M^+X^- exist in solution, the following relations can be established:

$$K(s)_{H_2O} = c_{M^+}c_{X^-} \qquad (12)$$

in dilute aqueous solution and

$$K(s)_{H_2O+NH_4NO_3} = c_{M^+}c_{X^-}f^{tr}_{M^+}f^{tr}_{X^-} \qquad (13)$$

in a concentrated $H_2O + NH_4NO_3$ medium. Relations 12 and 13 lead to

$$pK(s)_{H_2O+NH_4NO_3} - pK(s)_{H_2O} = \log f^{tr}_{M^+} + \log f^{tr}_{X^-} \qquad (14)$$

It thus appears that the solubility products of the MX salts can be calculated from eq 14 provided that the solvent transfer activity coefficients f^{tr} of the ions are known.

Experimental Section

Instrumentation. The normal potential of redox systems was determined using classical electrochemical methods: dc polarography and zero current potentiometry. The dc polarography was used in the cases of $Cd^{2+}/Cd(Hg)$, $Pb^{2+}/Pb(Hg)$, $Cu^{2+}/Cu(Hg)$, $Zn^{2+}/Zn(Hg)$, and $Sn^{2+}/Sn(Hg)$. For these systems the graphs were obtained with a classical three electrode setup and a Tacussel TI-PULS-EPL3 apparatus. Normal potentials were determined by zero current potentiometry at silver or platinum wire electrodes (Nernst's law) in the cases of Ag^+/Ag, AgX/Ag, Fe^{3+}/Fe^{2-}, and $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$. Those measurements were acquired on a Tacussel ISIS 20000 millivoltmeter. For the AgX/Ag systems, prior to the potentiometric measurements, AgX was deposited by controlled potential electrolysis on the silver electrode. The potentials were all measured at 298 K in comparison with the following reference electrode: aqueous standard calomel electrode (SCE) in a separated compartment containing 0.1 M of NH_4NO_3. As the potentials of all the systems are also quoted against the potential of the ferricinium/ferrocene couple in each solution, the junction potential between SCE and the working electrode does not take place.

Reagents. Ammonium nitrate (Riedel Del Haen, >98%) was used without further purification. The metallic salts are introduced in their nitrate form (Merck, <98%), the halides in their ammonium form (Merck, 98%).

Results and Discussion

Reference System: Ferricinium/Ferrocene. Strehlow's hypothesis about the ferricinium/ferrocene system is assumed to obtain the solvation transfer activity coefficients (*9*, *10*). Ferrocene (Fc) is only slightly soluble in $H_2O + NH_4NO_3$. Its blue-colored oxidized form, ferricinium (Fc^+), is readily obtained when the medium is sufficiently acidified in the presence of oxygen. However, its stability is low as it turns purple after about 30 min. Despite this short lifetime voltamograms at a polished gold electrode of Fc^+ in the $H_2O + NH_4NO_3$ solutions have been obtained. Voltamograms taken at different rotation rates show that the limiting currents increase linearly with the square root of the rotation rate predicted by Levich's equation (*17*). These findings clearly indicate that the Fc^+ reduction signal corresponds to a rapid and reversible system: the half-wave potential $E^1/_2$ value can therefore be regarded as the normal potential of the couple Fc^+/Fc. According to Strehlow, this potential is independent of the composition of the solutions. Experimentally, this value remains practically constant at 0.10 V against the SCE in the various $H_2O + NH_4NO_3$ solutions.

Solvation of Cations. The potentials in water and in different $H_2O + NH_4NO_3$ solutions are given in Table 1. The log f^{tr} values calculated from these potentials using relation 8 are summarized in Table 2. The examination of these results shows that the cations can be divided into two groups: The first group which includes Cu^{2+}, Cd^{2+}, and Zn^{2-} is characterized by positive and increasing values of log f^{tr} as the concentration of NH_4NO_3 increases. These cations are thus less solvated and consequently more reactive in the concentrated salt media since they are more oxidizing toward the ferrocene.

Nevertheless, the order that exists in a dilute solution is maintained for the whole concentration range studied here: E_0 (Zn^{2+}/Zn) < E_0 (Cd^{2+}/Cd) < E_0 (Cu^{2+}/Cu). The second group made of Ag^+, Pb^{2-}, Hg^{2+}, and Sn^{2+} includes cations whose reactivity decreases in the concentrated $H_2O + NH_4NO_3$ solutions since their oxidizing properties toward Fc decrease. They are characterized by negative values of

Table 1. Normal Potentials of Redox Systems in Aqueous Ammonium Nitrate Solutions (1–14 M), Referred to the Ferricinium/Ferrocene System

	$E^{\circ}_{H_2O+NH_4NO_3}$/mV							
	0.1 M	1 M	3 M	5 M	7 M	9 M	11 M	14 M
$Cu^{2+}/Cu(Hg)$	−140	−130	−120	−115	−110	−100	−95	−90
$Pb^{2+}/Pb(Hg)$	−500	−530	−570	−600	−620	−650	−700	−740
$Cd^{2+}/Cd(Hg)$	−780	−770	−765	−760	−750	−745	−740	−730
$Zn^{2+}/Zn(Hg)$	−1240	−1230	−1220	−1215	−1200	−1190	−1185	−1180
$Sn^{2+}/Sn(Hg)$	−510	−520	−540	−550	−560	−570	−580	−600
Hg^{2+}/Hg	+300	+248	+228	+215	+206	+198	+193	+191
Ag^+/Ag	+352	+329	+324	+313	+311	+301	+300	+296
AgCl/Ag	−104	−106	−107	−111	−112	−117	−119	−122
AgBr/Ag	−254	−261	−265	−266	−268	−269	−270	−273
AgI/Ag	−458	−471	−471	−475	−478	−480	−483	−488
Fe^{3+}/Fe^{2+}	+342	+346	+350	+356	+360	+368	+375	+377
$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$	+38	+79	+105	+113	+116	+119	+131	+135

Table 2. Solvent Transfer Activity Coefficients (log f^{tr}) of Ionic Species in Aqueous Ammonium Nitrate Solutions (1–14 M) (Strehlow Hypothesis)

ionic species	1 M	3 M	5 M	7 M	9 M	11 M	14 M
Cu^{2+}	0.35	0.70	0.85	1.00	1.40	1.55	1.70
Pb^{2+}	−1.00	−2.40	−3.45	−4.15	−5.20	−6.90	−8.30
Cd^{2+}	0.35	0.50	0.70	1.00	1.20	1.40	1.70
Zn^{2+}	0.35	0.70	0.85	1.40	1.70	1.90	2.05
Sn^{2+}	−0.35	−1.05	−1.40	−1.70	−2.10	−2.40	−3.10
Hg^{2+}	−1.80	−2.50	−2.90	−3.25	−3.50	−3.70	−3.75
Ag^+	−0.40	−0.50	−0.65	−0.70	−0.90	−0.90	−0.95
Cl^-	0.05	0.05	0.10	0.15	0.20	0.25	0.30
Br^-	0.15	0.20	0.25	0.25	0.25	0.30	0.35
I^-	0.25	0.25	0.30	0.35	0.40	0.45	0.50
Fe^{3+}/Fe^{2+}	0.10	0.15	0.25	0.30	0.45	0.60	0.60
$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$	0.70	1.15	1.30	1.35	1.40	1.60	1.70

log f^{tr} which evidence an interaction with ammonium nitrate. Although this interaction seems to be enhanced with Pb^{2+} and Sn^{2+}, it should be emphasized as a general feature that, for most species, the solvation varies only slightly with increasing salt concentration. This behavior probably arises from the lack of complexing with the nitrate anion. Studies have been performed on solvation properties of concentrated acids or salts. Results with concentrated HCl, chloride salts, H_3PO_4, and phoshate salts differ considerably from those observed in this study. Owing to the complexing character of the Cl^-, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} ions, the variation of solvation of many solutes is very large in these media (*6–8, 11, 12, 14–16*).

Solvation of Anions. The zero current potentiometry applied to the Ag^+/Ag, AgCl/Ag, AgBr/Ag, and AgI/Ag redox systems reveals that they obey the Nernst's law in all the salt solutions studied. An examination of their potential is reported in Table 1. It indicates an increase of the reducing character of silver toward ferricinium ions, the ferricinium/ferrocene system being used as the comparison system. This trend is held in the presence of halides. Under these conditions, the oxidation of Ag is easier in concentrated $H_2O + NH_4NO_3$ solutions than in H_2O. The studied halides are thus less solvated and consequently more reactive as the concentration of NH_4NO_3 increases. However, the variation of the solvation of the halides remains low.

Behavior of Fe^{3+}/Fe^{2+} and $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ Systems. Iron exists in many natural mineral products and influences the efficiency of the extraction of valuable species such as uranium or vanadium (*14*). Given that these species could be either oxidized or reduced by the iron species (a fact that determines the choice of the collector to be used during the flotation processes), the redox properties of the Fe(III)/Fe(II) system must be known. The preliminary result obtained in this study is the observation that the oxidation character of Fe(III) increases as the salt medium becomes concentrated (Tables 1 and 2). We are currently carrying on experiments in order to gain more insight into the reactivity of iron in its different oxidation states in $H_2O + NH_4NO_3$ mixtures, particularly the ability of ferric and ferrous ions to be complexed by solutes.

The behavior of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$system which is well known as an electrochemical indicator reveals also an increase in the oxidating character of hexacyanoferrate(III) in the concentrated medium (Tables 1 and 2).

Solubility and Solvation. Knowledge of log $f^{tr}_{M^-}$ and of log $f^{tr}_{X^-}$ leads to the prediction of the solubility of MX salt in $H_2O + NH_4NO_3$ mixtures. Results given in Table 3 are calculated from relation 15. They show that the solubility products of AgX do not change very much. This is due to the balance between two opposite effects: the increase of the solvation with Ag^+ and on the other hand the decrease observed with X^-. Similar results have already been obtained in concentrated phosphoric acid solutions neutralized or not by sodium hydroxide.

Table 3. pK(s) Values of AgX Salts in Aqueous Ammonium Nitrate Solutions (1–14 M)

	0.1 M	1 M	3 M	5 M	7 M	9 M	11 M	14 M
AgCl	9.75	9.70	9.50	9.35	9.40	9.35	9.35	9.35
AgBr	12.30	12.25	12.00	12.00	11.85	11.90	11.90	11.85
AgI	16.10	16.25	16.00	15.95	15.95	15.90	15.90	15.95

Conclusion

The solvation properties of aqueous ammonium nitrate solutions (1–14 M) of various redox systems not involving protons were measured. It appears that ammonium and nitrate ions interact weakly with the solutes.

The main conclusion is that the chemistry in these media is not strongly different from that in water and depends only slightly on the salt concentration.

The influence of the water activity on solute solvation and on partition equilibria involving immiscible organic solvents has to be studied for explaining the differences observed in liquid–liquid extraction of valuable mineral species in isopiestic aqueous solutions involving other electrolytes.

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