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Concentrated Hydrochloric Acid Media: Acid–Base, Oxidation–Reduction, and Solvation Properties

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The acidity level and the chloride anion activity are evaluated in H_2O-HCl mixtures (1.0 < |HCl| < 12.0 M) by means of Ro(H) and Ro(Cl^-) functions. For both functions, the potentials of the ferrocenium/ferrocene system (Fc^+/Fc) are used as reference potentials. Hydrogen and calomel electrodes are respectively employed for acidity level and chloride anion activity evaluations. It is shown that Ro(H) decreases from 0 to −6.2 and Ro(Cl^-) from 0 to −4.8 when HCl concentration increases from 1.0 to 12.0 M. Redox properties of some M^{n+}/M(Hg) couples (M^{n+} = Ag^+, Pb^{2+}, Cu^+, Sn^{2+}, Cd^{2+}) are examined. The solvation transfer activity coefficient (*f*) of ions M^{n+} are calculated with use of the standard potential values of the corresponding redox systems. M^{n+} ions, considerably solvated in H_2O-HCl mixtures (specific interactions with Cl^-) have a reactivity that varies very little with increasing HCl concentration. The *f* values for Ni^{2+} and Fe^{3+} determined from constants of liquid–liquid extraction show a desolvation of these ions with increasing HCl concentration.

Introduction

Hydrochloric acid is a widely used solvent because of its acidic and complexing properties and its low cost. It is extensively employed for the recovery of mineral products by liquid–liquid extraction, ion exchange, or ionic flotation.

Hydrochloric acid is also widely used for the dissolution of economically valuable ores. The acidity level of hydrochloric acid solutions regulates the extracting capacity of chelating agents used for immiscible systems. It also regulates the protonation of flotation agents as well as the redox properties of solutes.

Presented in this paper are the results of a study by electrochemical methods for H_2O-HCl mixtures (|HCl| from 1.0 to 12.0 M) giving the Ro(H) acidity function, the Ro(Cl^-) function characterizing Cl^- anion activity, and the solvation transfer activity coefficient (*f*) of solutes.

Along with water activities (a_{H_2O}) in H_2O-HCl mixtures, these results allow us to explain the changes with acid concentration of oxidation–reduction, precipitation reactions, and extraction processes.

Theoretical Aspects of Ro(H), Ro(Cl^-), Redox Properties, and *f* Coefficients

(1) Acidity Function Ro(H). The acidity function Ro(H) is obtained by the measurement of the hydrogen electrode potential versus the ferrocenium/ferrocene couple, whose standard potential is independent of the solvant (*1–6*), according to the relation

$$\mathrm{Ro(H)} = (E^{W}_{o}(\mathrm{H^+/H_2}) - E^{A}(\mathrm{H^+/H_2}))/0.058 \qquad (1)$$

with

$$E^{W}_{o}(\mathrm{H^+/H_2}) = -0.400 \text{ V vs } \mathrm{Fc^+/Fc}$$

(The superscript A corresponds to the acidic medium and the superscript W to water.)

(2) Cl^- Anion Activity Function Ro(Cl^-). By analogy with the acidity function Ro(H), Cl^- anion activity is characterized by the function Ro(Cl^-) (*7*, *8*). Ro(Cl^-) is determined from variations with acid concentration of redox potentials by using calomel electrode (Hg_2Cl_2(s)/Hg) according to the relation (from ref 9)

$$\mathrm{Ro(Cl^-)} = (E^{A}(\mathrm{Hg_2Cl_2(s)/Hg}) - E^{W}_{o}(\mathrm{Hg_2Cl_2(s)/Hg}))/0.029 \qquad (2)$$

(3) Redox Properties of H_2O-HCl Solution. From a thermodynamic point of view, the accessible potentials in the H_2O-HCl solutions are limited by oxidizing properties of the proton and reducing properties of water and the chlorides. These limits are given by potential variations of the H^+/H_2(g), O_2(g)/H_2O, and Cl_2(g)/Cl^- systems, with acid concentrations according to the relations

$$\mathrm{H^+/H_2(g)} \qquad E(\mathrm{V}) = -0.400 - 0.058\mathrm{Ro(H)} \qquad (3)$$

$$\mathrm{O_2(g)/H_2O} \qquad E(\mathrm{V}) = 0.830 - 0.058\mathrm{Ro(H)} - 0.029 \log a_{\mathrm{H_2O}} \qquad (4)$$

$$\mathrm{Cl_2(g)/Cl^-} \qquad E(\mathrm{V}) = 0.960 + 0.058\mathrm{Ro(Cl^-)} \qquad (5)$$

where all gases (H_2, O_2, and Cl_2) are at a pressure of 1 atm.

In oxidation, the limits are given first by O_2(g)/H_2O and then by Cl_2(g)/Cl^-, according to the relations

$$\Delta E(\mathrm{V}) = 1.230 - 0.029 \log a_{\mathrm{H_2O}} \qquad (6)$$

$$\Delta E(\mathrm{V}) = 1.360 + 0.058[\mathrm{Ro(Cl^-)} + \mathrm{Ro(H)}] \qquad (7)$$

In reduction, the limit is given by H^+/H_2(g), according to relation 3.

(4) Variations of Solute Solvation. Variations of solute solvation are characterized by means of the solvation transfer activity coefficients *f* (*10–12*). By convention, the notation M^{n+} is used in all cases, irrespective of the exact form of the species.

$f > 1$ (or $\log f > 0$) signifies that the species is less solvated in the solution under study than in water; on the other hand, $f < 1$ (or $\log f < 0$) signifies that the species is more solvated in the solution than in water.

The *f* coefficients are calculated from standard potential values of the corresponding redox systems according to relations 8 and 9. E^{W}_{o} represents the normal potential of the considered redox system in water. E^{A}_{o} is its value in a hydrochloric medium characterized by the acidity level Ro(H) (*9*, *12*) and the water activity a_{H_2O} (*13*). Both are referred to our reference

$$M^{n+}/M \text{ system} \qquad \log f(M^{n+}) = n(E^{A}_{o} - E^{W}_{o})/0.058 \qquad (8)$$

$$M^{n+}/M^{(n-m)+} \text{ system}$$

$$\log f(M^{N+}/M^{(n-m)+}) = m(E^{A}_{o} - E^{W}_{o})/0.058 \qquad (9)$$

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Table I. Standard Potentials[a] (±5 mV) of Redox Systems in Hydrochloric Acid Media (1.0–12.0 M)

	1.0 M	3.0 M	5.0 M	7.0 M	9.0 M	12.0 M
Fc^+/Fc	+100	+40	-20	-80	-122	-175
H^+/H_2	-299	-284	-269	-254	-238	-215
$Cd^{2+}/Cd(Hg)$	-740	-800	-860	-920		
$Cu^+/Cu(Hg)$	-235	-320	-385	-460	-502	-555
Cu^{2+}/Cu	+337	+317	+293	+280	+242	+220
$Pb^{2+}/Pb(Hg)$	-480	-545	-610	-672	-715	-770
$Sn^{2+}/Sn(Hg)$	-496	-560	-620	-672	-712	-752
Fe^{3+}/Fe^{2+}	+400	+355	+323	+271	+227	
Ag^+/Ag		+55	-15	-96	-140	-188
$Hg_2Cl_2(s)/Hg$	-32	-191	-304	-413	-494	-588

[a] Potentials are in millivolts and are referred to SCE in HCl 0.1 M.

system ferrocenium/ferrocene (Fc^+/Fc).

The f coefficients of extracted species have been determined from extraction constants.

If the extraction of a metallic cation M^{n+} with an acidic extractant HA in an organic solvent is considered, the extraction equilibrium

$$M^{n+} + n\overline{HA} \rightleftarrows \overline{MA_n} + nH^+ \qquad (10)$$

is characterized by the constant K:

$$K = \frac{[a(H^+)]^n\, a(\overline{MA_n})}{a(M^{N+})\, [a(\overline{HA})]^n} \qquad (11)$$

The f coefficients are calculated according to the relation

$$\log f(M^{n+}) = pK - pK^A_{app} - nRo(H) \qquad (12)$$

pK^A_{app} represents the equilibrium constant with an acidic aqueous phase characterized by its acidity level Ro(H).

This relationship is valid in any acidic mixture in which the extractive equilibrium remains unchanged and the nature of the organic phase unaltered when the composition of the acidic aqueous phase is modified.

Experimental Section

The standard potential of some redox systems were determined directly by means of classical electrochemical methods: dc polarography and zero-current potentiometry.

The dc polarography was used in the cases $Cd^{2+}/Cd(Hg)$, $Sn^{2+}/Sn(Hg)$, $Pb^{2+}/Pb(Hg)$, and $Cu^+/Cu(Hg)$.

Standard potentials are determined by potentiometry at silver and polished platinium electrodes (Nernst's law verification) in the cases Ag^+/Ag, Fe^{3+}/Fe^{2+}, and Cu^{2+}/Cu^+. The potentials were all measured at 20 °C by reference to the following electrode: aqueous saturated calomel electrode (SCE) in a separate compartment containing 0.1 M HCl.

Determinations of f values involving liquid-liquid extractive constants in H_2O-HCl media were carried out by following literature procedures.

Fe^{3+}, Ni^{2+}, and Y^{3+} were extracted respectively by nitrosophenylhydroxylamine (Cupferron) in chloroform (*14*), di-*n*-butyldithiophosphoric acid in carbon tetrachloride (*15*), bis(2-ethylhexyl)phosphoric acid in dodecane (*16*, *17*).

The functions Ro(H) and Ro(Cl^-), the thermodynamic limits, and the standard potentials (referred to the ferrocenium/ferrocene system) are given in Tables I–III. The solvation transfer activity coefficients (log f) are given in Table IV.

Table II. Potentials of Some Redox Systems, Ro(H), and Ro(Cl^-) in Hydrochloric Acid Media (1.0–12.0 M)

	H_2O	1.0 M	3.0 M	5.0 M	7.0 M	9.0 M	12.0 M
$E^A(H^+/H_2)$	-400	-399	-324	-249	-174	-116	-40
$E^A(Hg\ Cl_2(s)/Hg)$	-132	-132	-231	-284	-333	-372	-413
Ro(H)		0.0	-1.3	-2.6	-3.9	-4.9	-6.2
Ro(Cl^-)		0.0	-1.7	-2.6	-3.4	-4.1	-4.8
$-\log a_{H_2O}$		0.017	0.069	0.155	0.279	0.445	
$E(O_2/H_2O)$*	+830	+830	+905	+981	+1056	1114	
$E(Cl_2/Cl^-)$*	+960	+960	+861	+809	+763	+722	+682

[a] The different values of the parameters marked by an asterisk are calculated. All potentials are in millivolts (±5 mV) and are referred to the ferrocenium/ferrocene system.

Table III. Standard Potentials[a] (±5 mV) of Redox Systems in Hydrochloric Acid Media (1.0–12.0 M)

	H_2O	1.0 M	3.0 M	5.0 M	7.0 M	9.0 M	12.0 M
Ag^+/Ag	+400		+16	+5.0	-16	-18	-13
Fe^{3+}/Fe^{2+}	+370	+300	+315	+343	+351	+349	
$Cu^+/Cu(Hg)$	+121	-335	-360	-365	-380	-380	-380
Cu^{2+}/Cu^+	-240	+237	+273	+313	+360	+364	+395
$Pb^{2+}/Pb(Hg)$	-530	-580	-585	-590	-592	-593	-595
$Sn^{2+}/Sn(Hg)$	-540	-596	-600	-600	-592	-590	-577
$Cd^{3+}/Cd(Hg)$	-800	-840	-840	-840	-840		

[a] Potentials are in millivolts and are referred to the ferrocenium/ferrocene system.

Table IV. Solvation Transfer Activity Coefficients in Hydrochloric Acid Media (1.0–12.0 M)[a]

	1.0 M	2.0 M	3.0 M	4.0 M	5.0 M	7.0 M	9.0 M	12.0 M
log $f(Y^{3+})$*	1.3	2.8		6.1	9.6			
log $f(Ni^{2+})$*	0.9		1.4		3.5	5.8	7.5	
log $f(Cd^{2+})$	-1.4		-1.4		-1.4	-1.4		
log $f(Sn^{2+})$	-1.9		-2.1		-2.1	-1.8	-1.7	-1.3
log $f(Pb^{2+})$	-1.7		-1.9		-2.1	-2.1	-2.2	-2.2
log $f(Ag^+)$			-6.6		-6.8	-7.2	-7.2	-7.1
log $f(Fe^{3+}/Fe^{2+})$	-1.2	-1.0	-0.9	-0.6	-0.5	-0.3	-0.4	
log $f(Fe^{3+})$*	-1.5	0.5	1.5	2.8				
log $f(Fe^{2+})$	-0.3	1.5	2.4	3.4				
log $f(Cu^{2+}/Cu^+)$	8.2		8.8		9.4	10.3	10.4	10.9
log $f(Cu^+)$	-7.9		8.3		-8.4	-8.6	-8.6	-8.6
log $f(Cu^{2+})$	0.3		0.5		1.6	1.7	1.8	2.3

[a] The different values of the parameter marked with an asterisk are calculated from relation 12.

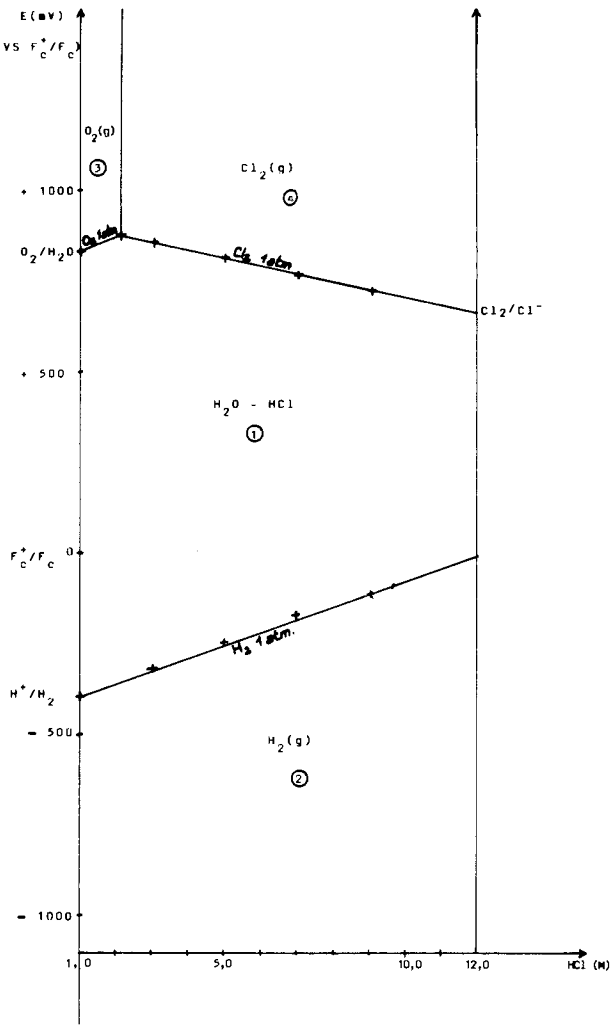

Figure 1. Potential-concentration diagram in hydrochloric acid media ($1.0 \leq HCl \leq 12.0$ M).

Discussions

The acidity level in hydrochloric acid media (1.0-12.0 M) ranges over six units (0 to -6.2) and the Cl^- anion activity from 0 to -4.8.

The comparison carried out by using the Ro(H) acidity function in $H_2O-H_2SO_4$ (*4*), H_2O-HCl (*9*, *12*), H_2O-HF (*8*), and $H_2O-H_3PO_4$ (*5*, *6*, *11*) leads to the conclusion that, for the same value of water activity, these acids and their mixtures (*18*) are characterized by the same Ro(H) acidity level and have identical oxidizing properties.

In reduction, reactions are limited by the reduction of H^+ according to relation 3.

In oxidation, reactions are limited by the oxidation of water, and chlorides according to relations 4 and 5. The graphs plotted with these relations show a convergence at $|HCl| = 2.4$ M (Figure 1). For $|HCl| < 2.4$ M, oxidation of water to oxygen predominates, and for $|HCl| > 2.4$ M, the Cl^- anion is oxidized to Cl_2 and limits the reactions. The thermodynamic range decreases from 1.230 to 0.722 V when the HCl concentration increases from 1.0 to 12.0 M. This is very different from that of other H_2O-acid (H_2SO_4, H_3PO_4, $HClO_4$) solutions where the range is given by relation 6. At high concentrations the term 0.029 log a_{H_2O} is very low and can be neglected. The range is nearly constant about 1.230 V.

Cu^+, Ag^+, Sn^{2+}, Pb^{2+}, and Cd^{2+} are characterized in H_2O-HCl media by negative log *f* values, indicating a specific interaction with hydrochloric acid. These species are more solvated (thus less reactive) in hydrochloric acid media than in water. Their reactivity varies slightly with increasing acidity. This property leads to considerable consequences in the prediction of reactions of liquid-liquid extraction, ion-exchange, or ionic flotation in hydrochloric acid solutions.

Cu^+, Ag^+, Sn^{2+}, Pb^{2+}, and Cd^{2+} are probably in the form of the soluble complexes $CuCl_2^-$, $AgCl_2^-$, $SnCl_3^-$, $PbCl_3^-$, and $CdCl^+$. The order of their solvation is similar to that of their p*K* in water (*19*).

Fe^{3+}, Fe^{2+}, Ni^{2+}, Y^{3+}, and Cu^{2+} have increasing positive values of log *f*. They are less solvated and more reactive in the more concentrated hydrochloric acid media. At the same acidity level, log *f* values increase with the number of cationic charges.

A desolvation of these ions with increasing acid concentration is observed; this desolvation compensates in part for the effect of the acidity level, which is considerable as two or three protons participate in the equilibrium (*12*). The increase of the oxidizing power of the corresponding systems is related to the considerable desolvation of the cation with acid content.

At low concentrations of $|HCl| < 1.0$ M, Fe^{3+}, Fe^{2+}, Ni^{2+}, and Y^{3+} have negative log *f* values, indicating a specific interaction with hydrochloric acid, HCl.

Glossary

Ro(H)	Strehlow's acidity function
$Ro(Cl^-)$	chloride anion activity
$f(M^{n+})$	solvation transfer activity coefficient of the M^{n+} ion
$f(M^{n+}/M^{(n-m)+})$	solvation transfer activity coefficient of the $M^{n+}/M^{(n-m)+}$ system
a_{H_2O}	water activity
E_0^W	standard potential in water
E^A	potential in acidic medium
E_0^A	standard potential in acidic medium
$\overline{HA}$	acidic extractant in an organic phase
$\overline{MA}$	extracted cation in an organic phase
p*K*	equilibrium constant in water
pK_{app}^A	equilibrium constant in an acidic aqueous phase

Registry No. HCl, 7647-01-0; Cl^-, 16887-00-6.

Literature Cited

(1) Koepp, H. M.; Wendt, H.; Strehlow, H. *Z. Electrochem.* **1960**, *64*, 483.
(2) Strehlow, H. In *The Chemistry of non-aqueous solvents*; Lagowski, J. J., Ed.; Academic Press: New York, 1966; Vol. I, Chapter 4, p 129.
(3) Vaillant, A.; Devynck, J.; Tremillon, B. *Anal. Lett.* **1973**, *6* (12), 1095.
(4) Bauer, D.; Bouchet, M. *C. R. Acad. Sci., Ser. C.* **1972**, *275* (1), 21.
(5) Louis, C.; Bessiere, J. *Anal. Lett.* **1980**, *13* (A11), 937.
(6) Louis, C.; Bessiere, J. *Can. J. Chem.* **1985**, *63* (4), 908.
(7) Menard, H.; Masson, J. P.; Devynck, J.; Tremillon, B. *J. Electroanal. Chem.* **1974**, *63*, 163.
(8) Vaillant, A.; Devynck, J.; Tremillon, B. *J. Electroanal. Chem.* **1974**, *57*, 219.
(9) Babale, D. Thèse de Doctorat de Troisième cycle, University of Yaounde, Yaounde, Cameroun, 1981.
(10) Louis, C.; Bessiere, J. *Can. J. Chem.* **1986**, *64*, 608.
(11) Louis, C.; Bessiere, J. *J. Chem. Eng. Data* **1986**, *31*, 472.
(12) Babale, D. Thèse de Doctorat d'Etat, University of Yaounde, Yaounde, Cameroun, 1987.
(13) Coussemant, F.; Hellin, M.; Torch, B. *les Fonctions d'acidité et leurs utilisations en catalyse acido-basique*; Gordon and Breach: Paris, London, New York, 1969.
(14) Benayada, A. Thèse de Doctorat d'Etat, University of Nancy I, Nancy, France, 1986.
(15) Sabot, J. L. Thèse de Doctorat d'Etat, University of Paris VI, Paris, France, 1978.
(16) Owens, T. C.; Smutz, M. *J. Inorg. Nucl. Chem.* **1968**, *30*, 1617.
(17) Michelsen, O. B.; Smutz, M. Contribution no. 2727 from Ames Laboratory, U.S. Atomic Energy Commission, Ames, IA. 1970.
(18) Louis, C.; Bebba, A.; Bessiere, J. *Can. J. Chem.* **1987**, *65*, 1353.
(19) Charlot, G. *L'analyse qualitative et les réactions en solution*; Masson: Paris, 1963.

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