1214 *J. Chem. Eng. Data* **2003,** *48,* 1214−1220

Electrochemistry in Concentrated Hydrochloric Acid ($C \leq 5$ M) Progressively Neutralized by Sodium Hydroxide Pellets: Acid−Base, Oxidation−Reduction, and Solvation Properties of the Medium

Emmanuel Ngameni,[†] Charles Péguy Nanseu-Njiki,[†] Roland Wandji,[†] and Jacques Bessiere*[,‡]

Laboratoire de Chimie Analytique, Faculté des Sciences, Université de Yaoundé I, B.P. 812 Yaoundé-Cameroun, and Laboratoire de Chimie Physique et Microbiologie pour l'Environnement, UMR 7564 CNRS, Université H. Poincaré, Nancy 1, 54600 Villers lès Nancy, France

The acid−base and oxidation−reduction properties of aqueous HCl + NaCl mixtures (HCl + NaCl ≤ 5 M) are characterized by means of the Ro(H) acidity function and the Ro(Cl^-) function, which respectively represent their ability to give up the proton and the chloride ion. The electrochemical windows of these mixtures at various working electrodes including mercury drop, carbon, platinum, and gold are determined. The solvation properties of these media are characterized by means of the solvation transfer activity coefficients of the solutes, which are calculated from the normal potential values of the corresponding redox system.

1. Introduction

The physicochemical properties of concentrated media have been the subject of several studies over the past three decades mainly because of their implication in various industrial processes. In fact, concentrated mineral acids are widely used in processes such as metal pickling and chemical polishing of crystal. In the field of hydrometallurgy, these media are recommended for the recovery of valuable species (uranium, gold)[1,2] by liquid−liquid extraction, ion exchange, or ionic flotation or for the elimination of toxic heavy metals (cadmium, lead, arsenic, etc.) generally present in metal ores.[3,4] This is the case for highly concentrated phosphoric acid solutions produced in the industrial processing of phosphate ores. Highly concentrated media are also used as raw materials for the synthesis of numerous industrial products such as fertilizers and other chemicals (detergents, organic reagents, food products).[5]

Improvement of any of these processes requires the knowledge of the thermodynamic data of the media as well as their complexing properties. Knowledge of these data, which include acidity level, redox properties, and water activity, permits the forecasting of changes in the extracting properties of chelating agents used for liquid−liquid phenomena, such as the protonation of collectors involved in flotation operations.

Concentrated media with various compositions have been the subject of experiments so far, and it appears that salt solutions of various acidity levels are among the most convenient.[6] As a matter of fact, concentrated chloride media are often used in hydrometallurgy either in their hydrogen form or in their alkaline-earth form. The knowledge of their chemical properties in view of a better understanding of the behavior of solutes thus appears as a matter of crucial scientific interest. This work seeks to study the evolution of the acid−base, redox, and solvation properties of concentrated hydrochloric acid solutions when sodium hydroxide is progressively added to the medium; some emphasis is put on the role of the resulting salt, NaCl. The paper also aims at showing what interesting and valuable tools electrochemical techniques are, when dealing with solution phenomena.

2. Experimental Section

2.1. Reagents. All chemicals used were of analytical reagent grade and were used without further purification. Hydrochloric acid and sodium hydroxide pellets were purchased from Riedel de Haen, ferrocene was from Sigma, and 3,4,5,6-tetrachloro-1,2-benzoquinone (*o*-chloranil) was from Fluka.

2.2. Preparation of Solution. The neutralization procedure was as follows:

The starting 5 M hydrochloric acid was placed in a flask, and the sodium hydroxide pellets were progressively added until the desired neutralized ratio was reached. The neutralization level defined by the molar ratio Na/H varies from 0.0 to 1.0. During this operation, the solution was continuously stirred under reflux to prevent the evaporation of its contents.

The oxidized form of ferrocene, ferricenium, was obtained by allowing the former to react with 3,4,5,6-tetrachlora-1,2-benzoquinone in the two phase medium: H_2O + HCl + NaCl/toluene.

The paste was prepared according to Adam's procedure:[7−9] the carbon and the quinone were mixed in a 1:1 wt ratio and formulated with Nujol (15 wt %) to form a paste.

For the Ro(Cl^-) experiment, a mercury J electrode on which Hg_2Cl_2 was deposited by controlled potential electrolysis was used.

2.3. Equipment. The zero current potentiometry measurements were made by using a TACUSSEL ISIS 20000 millivoltmeter. The voltammetric graphs were obtained with a classical three electrode setup and a TACUSSEL TI-PULS-EPL3 apparatus. The working electrode consisted of a mercury drop, a disk (platinum, gold, carbon), or a carbon paste adaptable to the EDI controvit TACUSSEL unit for the RDE experiments. A commercial fiber-plug

---

[†] Université de Yaoundé I.

[‡] Université H. Poincaré.

10.1021/je0301343 CCC: $25.00

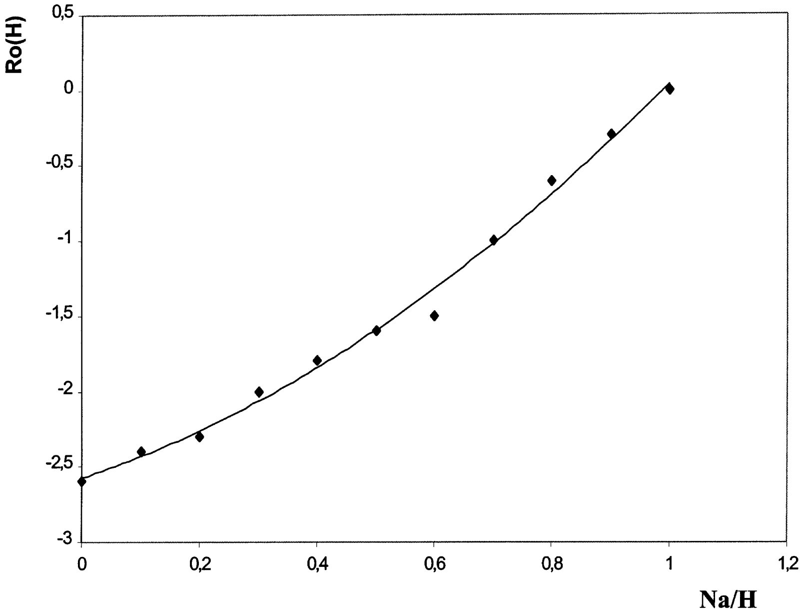


Figure 1. Variation of the Ro(H) function in 5 M hydrochloric acid progressively neutralized by sodium hydroxide.

saturated calomel electrode (SCE) in a separate compartment containing 0.1 M hydrochloric acid was used as the reference electrode while the auxiliary electrode was made of a platinum wire. The uncertainty on the values of the measured potentials is ±5 mV.

3. Results and Discussions

3.1. Ro(H) Acidity Function for $H_2O + HCl + NaCl$ Media. The characterization of the acidity level in concentrated media cannot be achieved by performing the classical direct potentiometric measurement that implies the determination of the potential of a pH indicating system, referred to the SCE. As a matter or fact, each mixture $H_2O + HCl + NaCl$ can be viewed as a solvent on its own, with its proper potential scale. The comparison between the various potentials thus requires a common reference whose potential does not depend on the nature of the solvent. Strehlow and others[10] showed that an acceptable approximation can be achieved with some metallocenes such as ferrocence (Fc), given their interesting structure that is voluminous and almost spherical and which implies a quasi identical structure for the related cation: the ferricenium. The authors therefore assume that Fc and Fc^+ are equally solvated in the various $H_2O + HCl + NaCl$ mixtures. The acidity function Ro(H) derived from the above assumption is experimentally obtained from measurements in which the potential of an appropriate quinone/hydroquinone redox system is quoted against the potential of the ferrocene/ferricenium redox system.

3.1.1. Redox Behavior of the Comparison System: Fc. The examination of the redox behavior of Fc^+ cation in the neutralized $HCl + H_2O$ media leads to the following electrochemical characteristics: rapid transfer of electrons and reversibility on platinum, gold, and carbon electrodes. A single signal related to the reduction of Fc^+ is observed during the RDE experiment on Fc^+ solution in these media. Classical calculations derived from these voltammetric curves lead to slopes that vary between 55 and 60 mV. Accordingly, the half wave potentials ($E_{1/2}$) reported during the experiment were regarded as the normal potential of the system Fc^+/Fc.

3.1.2. Redox Behavior of the Quinone/Hydroquinone Redox System. As evidenced by the following equation, providing that the potential of the quinone (Q)/hydroquinone (QH_2) system is measurable in a given medium, this redox system is a convenient proton indicator: its potential, of course, does depend only on the acidity level:

$$Q(s) + 2H^+ + 2e \rightleftharpoons QH_2(s) \qquad (1)$$

Generally, the potential of the Q/QH_2 system in concentrated media is obtained by the carbon paste electrode technique. This is the case for the concentrated phosphoric media,[6,9,11−12] for which the zero current potential obtained with a carbon paste electrode that comprises both chloranil and hydrochloranil (Q, QH_2) is well defined and perfectly stable. By contrast, in the present work, a different behavior is observed with the neutralized HCl. Indeed, the mixture in the paste, when put in contact with the $H_2O + HCl + NaCl$ media, exhibits poor stability as part of the quinone gets dissolved. Yet the quantity in solution is rather low. However, this low quantity appears to be sufficient for electrochemical purposes. The corresponding voltammetric trace reveals that the solution consists of a mixture of *o*-chloranil and hydrochloranil, the electrochemical behavior of which corresponds to a rapid system; the potentials obtained from the zero current potentiometry are perfectly stable within the entire range of Na/H.

The Ro(H) values derived from experimental measurements related to the systems Q/QH_2 and Fc^+/Fc according to relation 2 are reported in Figure 1.

$$\mathrm{Ro(H)} = \frac{E^{H_2O}_{Q(s)/QH_2(s)} - E^{S}_{Q(s)/QH_2(s)}}{0.058} \qquad (2)$$

One can notice that the acidity level is lowered up to 2.5 units when the ratio Na/H is raised from 0.0 to 1.0. Of course, this is essentially due to the addition of sodium hydroxide pellets, although Bessiere et al.[6] assigned part of this decrease to the water that originates from the neutralization process itself.

Another point of interest is the effect of the salt NaCl on the acidity level expressed by Ro(H). Babale et al.[13] previously described the behavior of $H_2O + HCl$ mixtures ($1.0\ M < |HCl| < 12.0\ M$). On comparing their results with the present work, it appears that, for a given HCl content,

Table 1. Comparison of the Ro(H) Values for (1) the Neutralized 5 M Hydrochloric Acid Medium and (2) the Corresponding Diluted Solutions[13]

Na/H	0.0	0.2	0.4	0.6	0.8
acid concentration (mol·L−1)	5.0	4.0	3.0	2.0	1.0
Ro(H) (1)	−2.6	−2.3	−1.8	−1.5	−0.6
Ro(H) (2)	−2.6	−2.1	−1.5	−0.9	−0.2

the $H_2O + HCl + NaCl$ medium has a higher acidity than the $H_2O + HCl$ one. Hence, for instance, in a solution of $H_2O + HCl + NaCl$ for which Na/H = 0.2, which corresponds to an HCl content of 4 M (see Table 1), Ro(H) = −2.3, while, for an $H_2O + HCl$ mixture in which |HCl| = 4 M, Ro(H) = −2.1. This observation, which implies that the proton has a higher activity in a medium enriched with chloride, matches Lucas' conclusion concerning a study of the behavior of concentrated lithium chloride solutions[14] and that of Sella for $HCl + H_2O + MCl_n$ mixtures.[15]

3.2. Cl^- Anion Activity Function Ro(Cl^-). By analogy with the acidity function Ro(H), Cl^- anion activity is characterized by the function Ro(Cl^-).

Ro(Cl^-) = $-\log a_{Cl^-}$ expresses the ability of a $H_2O + HCl + NaCl$ mixture to release the Cl^- ion. The experimental procedure for obtaining Ro(Cl^-) relies on a rather general principle convenient for every concentrated mixture (water−acid or water−salt). This procedure consists of the measurement of the potential of an electrode whose implementation implies a unique soluble species, precisely the one whose activity ought to be monitored.

Hence, given the following redox equilibrium (eq 3),

$$Hg_2Cl_2(s) + 2e \rightleftharpoons 2Hg(s) + 2Cl^- \quad (3)$$

the potential of the system $Hg_2Cl_2(s)|Hg(s)$ depends solely on the species Cl^-, according to the relation (eq 4)

$$E_{H_2O+HCl+NaCl} = E^\circ_{H_2O} + \frac{0.058}{2}\log a_{Cl^-} \quad (4)$$

from which Ro(Cl^-) is deduced:

$$Ro(Cl^-) = \frac{E_{H_2O+HCl+NaCl} - E^\circ_{H_2O}}{0.029} \quad (5)$$

So, for the same reference ($Fc^+|Fc$ used), the variation between the two potential values of $Hg_2Cl_2(s)|Hg(s)$ measured in H_2O on one hand and in the neutralized HCl on the other hand leads to Ro(Cl^-).

The values of Ro(Cl^-) obtained with a J electrode on which Hg_2Cl_2 is deposited by controlled potentiometry are depicted in Figure 2. A slight increase in the reducing power of Hg is noted for 0.0 < Na/H < 0.5. Interestingly, Ro(Cl^-), which diminishes up to 0.6 units in the above range, does not vary any more during the second half of the neutralization process. So, the activity of Cl^- increases slightly at the beginning of the neutralization and gets stabilized afterward. Yet the amount of chloride does not change from Na/H = 0 till Na/H = 1. However, the composition of the medium varies to a large extent, from $H_2O + HCl$ (Na/H = 0.0) to $H_2O + HCl + NaCl$ (0.0 < Na/H < 1.0) and then to $H_2O + NaCl$ (Na/H = 1.0).

The observation that the presence of the chloride in the medium leads to a rather slight increase in the activity of Cl^- is not surprising: in previous studies Bates and Majima[16,17] indicated that, although the addition of MCl_n in HCl leads to the diminution of free water (that is, the water which is not involved in the hydration of ions or molecules), only the cation H^+ is affected by the phenomenon; the anion Cl^- has a rather poor affinity to H_2O.[15] One salient and interesting result to be underlined from the present work is that $Hg_2Cl_2(s)|Hg(s)$ is suitable as a comparison system in the neutralized HCl, for which Na/H ≥ 0.5, given that Ro(Cl^-) or the activity of Cl^- remains constant in that zone.

Attempts to obtain Ro(Cl^-) from the system $AgCl(s)|Ag(s)$ were unsuccessful: although this redox system appears to fulfill the criterion of being a Cl^- indicator, the experimental measurement was not conclusive because of poor stability of the salt AgCl(s). AgCl(s) probably slowly gets transformed into more soluble species ($AgCl_2^-$, $AgCl_3^{2-}$) since the medium is so rich in chloride.

3.3. Redox Properties of the $H_2O + HCl + NaCl$ Mixtures. The electrochemical windows of the various $H_2O + HCl + NaCl$ mixtures at various working electrodes including mercury drop, platinum, carbon, and gold were determined.

It is apparent from Table 2 that this window is somehow a bit larger as the H_2O-HCl solution gets neutralized. The increase for mercury, gold, and platinum is 0.25 V as Na/H varies from 0.0 to 1.0; the corresponding value for carbon is higher: 0.70 V.

From a thermodynamic point of view, the accessible potentials in the $H_2O + HCl + NaCl$ mixtures should be limited by the oxidizing properties of the protons and the reducing properties of water and the chlorides.

In oxidation, the limit may be due to O_2 or Cl^-, whose oxidation varies with the acid concentration according to the relations (eqs 6 and 7)

$O_2(g)|H_2O$:

$$E/V = 0.830 - 0.058\ Ro(H) - 0.029\log a_{H_2O} \quad (6)$$

$$Cl_2(g)|Cl^-: \quad E/V = 0.960 + 0.058\ Ro(Cl^-) \quad (7)$$

where O_2 and Cl_2 are at the pressure of 1 bar and 0.830 V and 0.960 V are the values of the normal potential versus ferrocene/ferricenium for O_2/H_2O and $Cl_2|Cl^-$, respectively.

As one could expect from the above equation, a slight increase of the accessible potential in oxidation is observed (Table 2) at all the solid electrodes examined as Na/H increases. However, this table also shows that, in accordance with what is generally found in concentrated aqueous acid or salt solutions,[3,13] the early oxidation of the mercury electrode observed in the present study, rather than the thermodynamic limitation, does constitute the effective solvent breakdown. This of course precludes polarography from any use when one is interested in analyzing oxidative species in the neutralized HCl media.

As one could expect, in reduction, the mercury electrode offers the largest potential limit, confirming the prominent role of polarography as far as the analysis of reductive species is concerned. Thermodynamically, the limit in reduction is given by the H^+/H_2 system according to the relation (eq 8)

$$E/V = -0.400 - 0.058\ Ro(H) \quad (8)$$

Table 2 also reveals that the proton reduction overpotential is rather weak on gold as well as on platinum while carbon and mercury offer the largest overpotential and electrochemical window, especially for the highest Na/H ratios.

3.4. Solvation Properties. Variation of solute solvation is characterized by means of the solvation transfer activity coefficient f^{tr}.[3,18] The f^{tr} coefficients can be obtained from

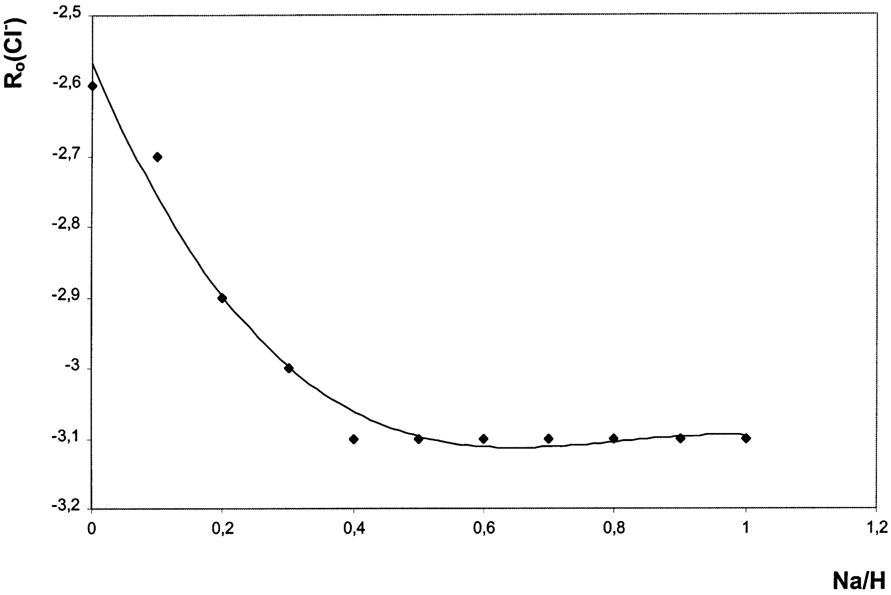


Figure 2. Variation of the Ro(Cl^-) function in 5 M hydrochloric acid progressively neutralized by sodium hydroxide.

Table 2. Electrochemical Windows (±5 mV) of Working Electrodes (Mercury Drop, Platinum, Carbon, and Gold) in 5 M Hydrochloric Acid Solution Neutralized by Sodium Hydroxide

	Na/H:	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Hg	E_a/mV	−80	−85	−90	−100	−100	−115	−120	−125	−130	−130	−130
	E_c/mV	−1080	−1095	−1120	−1155	−1190	−1230	−1250	−1280	−1300	−1320	−1340
	ΔE/mV	1000	1010	1030	1055	1090	1115	1130	1155	1170	1210	1230
Au	E_a/mV	560	580	580	590	590	600	620	630	630	610	590
	E_c/mV	−190	−210	−220	−230	−250	−260	−270	−290	−310	−350	−410
	ΔE/mV	750	690	800	820	840	860	860	920	940	960	1000
Pt	E_a/mV	860	870	880	890	890	890	890	920	950	945	920
	E_c/mV	−170	−190	−210	−230	−250	−270	−280	−290	−310	−330	−370
	ΔE/mV	1030	1060	1090	1120	1140	1160	1170	1210	1260	1275	1290
Cv	E_a/mV	1000	1005	1000	1025	1040	1030	1045	1030	1050	1050	1090
	E_c/mV	−430	−495	−540	−585	−640	−710	−770	−840	−900	−970	−1050
	ΔE/mV	1430	1500	1540	1610	1680	1740	1815	1870	1950	2020	2140

the standard potential values of the corresponding redox systems. Given the following oxidation−reduction (eq 9),

$$A + ne \leftrightarrows B \tag{9}$$

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 the expression (eq 10)

$$E_{H_2O} = E^\circ_{H_2O} + \frac{0.059}{n}\log\frac{C_A}{C_B} \tag{10}$$

where C_A and C_B are the molar concentrations of the solutes and the normal potential $E^\circ_{H_2O}$ is being compared with the ferricenium/ferrocene system chosen as the reference potential. In a neutralized hydrochloric medium, with the molar concentrations of A and B being kept low and in the same range, the potential of the couple A/B is

$$E_{H_2O+HCl+NaCl} = E^\circ_{H_2O} + \frac{0.059}{n}\log\frac{C_A}{C_B} + \frac{0.059}{n}\log\frac{f_A^{tr}}{f_B^{tr}} \tag{11}$$

where f_A^{tr} and f_B^{tr} are the solvent transfer activity coefficients of species A and B, respectively, from the aqueous solution taken as reference to the neutralized hydrochloric solution.

The redox couple A/B is therefore characterized in the H_2O + HCl + NaCl media by the normal potential $E^\circ_{H_2O+HCl+NaCl}$ given by eq 12:

$$E^\circ_{H_2O+HCl+NaCl} = E^\circ_{H_2O}\frac{0.059}{n}\log\frac{f_A^{tr}}{f_B^{tr}} \tag{12}$$

So the ratio f_A^{tr}/f_B^{tr} does depend only on the difference between the potential of the couple A/B in H_2O + HCl + NaCl and that in H_2O. In the particular cases of the redox system of the type

$$M^{n+} + ne \rightarrow M(s) \tag{13}$$

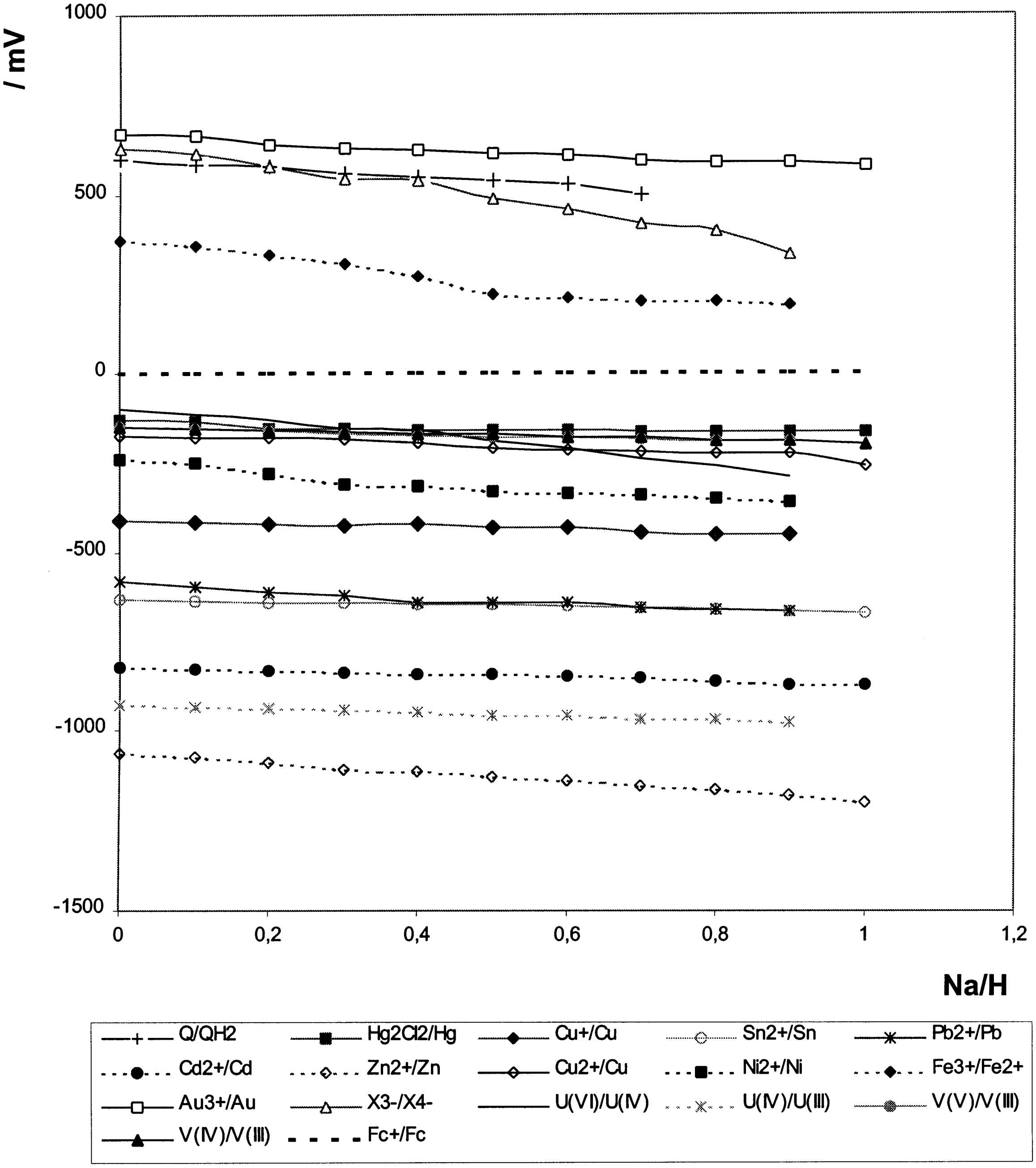
$$M^{n+} + me \rightarrow M^{(n-m)+} \tag{14}$$

where (s) indicates the solid species, eq 12 takes the forms of eqs 15 and 16:

$$E^\circ_{H_2O+HCl+NaCl} = E^\circ_{H_2O} + \frac{0.059}{n}\log f^{tr}_{M^{n+}} \tag{15}$$

$$E^\circ_{H_2O+HCl+NaCl} = E^\circ_{H_2O} + \frac{0.059}{n}\log\frac{f^{tr}_{M^{n+}}}{f^{tr}_{M^{(n-m)+}}} \tag{16}$$

Figure 3 shows the evolution of the behavior of various redox systems with the neutralization process. The normal potential values of the considered redox systems were measured directly by means of classical electrochemical methods: (a) dc polarography, (b) zero current potentiometry, and (c) voltammetry at rotating disk electrodes



X = $Fe(CN)_6$

Figure 3. Normal potential of redox systems in 5 M hydrochloric acid progressively neutralized by sodium hydroxide, referred to the Fc^+/Fc system.

(platinum, gold, and carbon). In the case of a rapid system, normal potentials and half-wave potentials are considered equal while the diffusion coefficients of cations in the solution and in the amalgam are the same. The potential–Na/H diagram in Figure 3 corresponds to a graphic illustration of the solvation phenomena, since the activity data are obtained from electrochemical measurements. This diagram shows (i) the implication of the acidity level, the water activity, on the reactivity of species in the HCl–NaCl mixtures and (ii) the solvation of the oxidized relative to the reduced form of the various couples. This graph also enables the prediction of the feasibility of the oxido-reduction reaction in these media. In the present case, one can observe that when HCl gets neutralized, a comparable slight variation in the potential of the different systems occurs. Apart from Fc^+/Fc, all the species examined exhibit an increase in the reductive power of the reduced form of the couple.

The various transfer activity coefficients calculated in the cases where the corresponding data were available using eqs 15 and 16 are plotted versus the neutralization ratio Na/H in Figure 4. The common trend is that these cations are more solvated in the neutralized media than in water. They are indeed characterized by negative values of log f^{tr}, which of course reveal lower reactivity as the acid gets neutralized. Given that the various systems examined are not involved in complexation phenomena in water (the reference solvent), when the ionic strength is increased (5 M HCl), these species should be less reactive. This is indeed observed through the negative log f^{tr} values obtained before any addition of sodium hydroxide. On neutralizing the 5 M HCl medium, one observes, as a common trend, only a

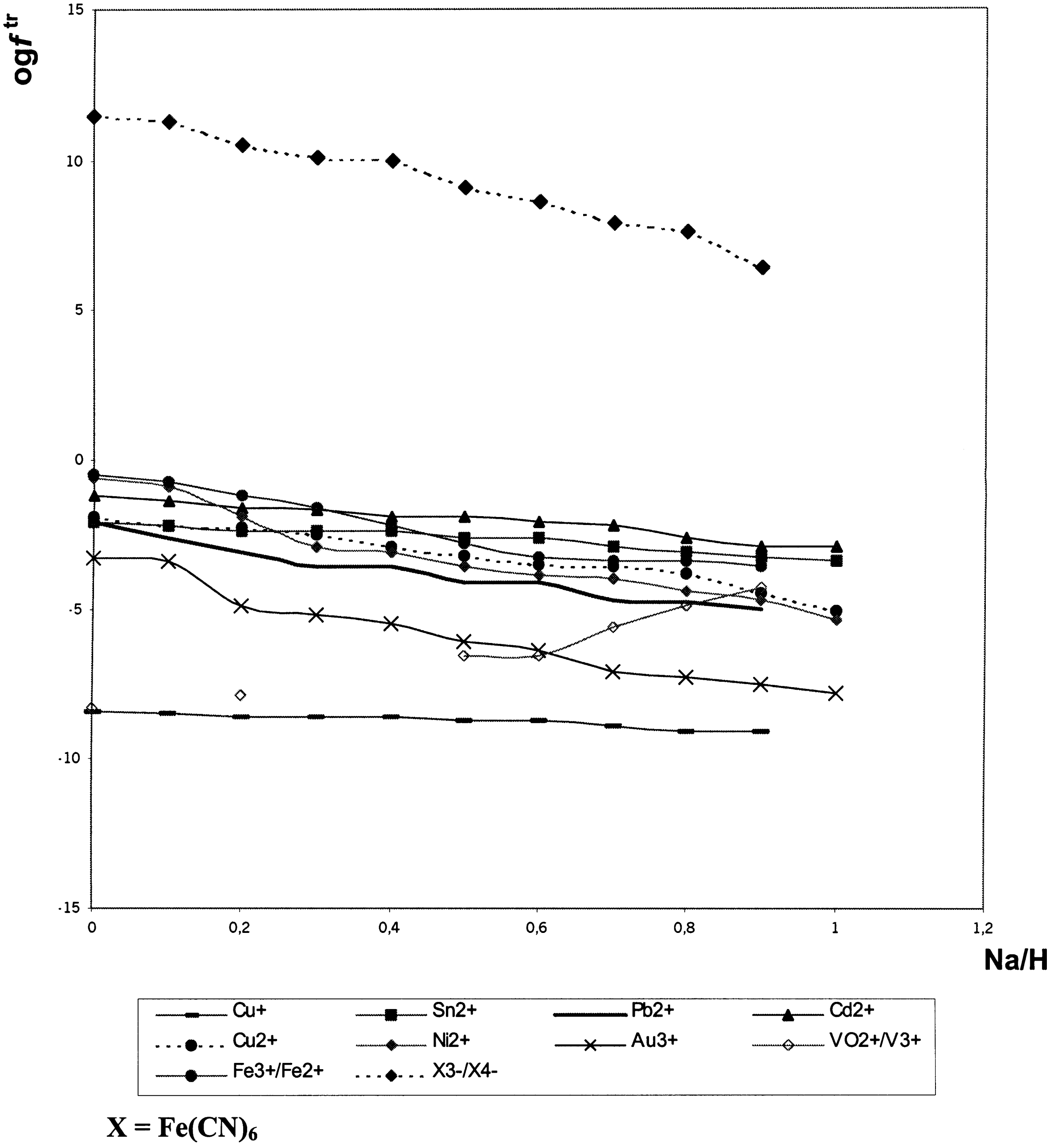


Figure 4. Solvation transfer activity coefficients of ionic species in 5 M hydrochloric acid progressively neutralized by sodium hydroxide.

slight variation in the log $f^{tr}_{M^{n+}}$ values. This can be explained by the fact that the amount of chloride in the medium does not vary during the neutralization process.

The solvation effect on a proton-dependent system VO^{2+}/V^{3+} was also examined. This system involves two protons in its redox process. In the starting medium ([HCl] =5 M), the ratio log f^{tr}_{ox}/log f^{tr}_{red} is rather high. Its negative value indicates that the solvation is higher for the oxidized form. The neutralization results in the lowering of the solvation effect, although the oxidized form remains in all cases the most affected: a fact which implies that this form displays a bigger interaction with Cl^- than the reduced one.

The well-known electrochemical indicator system $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ exhibits high positive values of log f^{tr}_{ox}/log f^{tr}_{red}. The solvation of an anion depends on both its basicity and its charge; it is well-known that $Fe(CN)_6^{3-}$ has no base property by contrast with $Fe(CN)_6^{4-}$; the latter is then more solvated in the neutralized HCl than its oxidative counterparts.

4. Conclusion

The acid−base, oxidation−reduction, and solvation properties of HCl + NaCl mixtures resulting from the progressive neutralization of 5M HCl by sodium hydroxide pellets were examined. The acidity level given by the acidity function Ro(H) is lowered up to 2.5 units when the neutralization level defined by the molar ratio Na/H is raised from 0.0 to 1.0. Ro(Cl^-), the ability of the media to give up the chloride ion diminishes up to 0.6 units for 0.0 < Na/H < 0.5, but it does not vary any more during the second half of the neutralization process. The Ro(Cl^-) indicating system $Hg_2Cl_2/Hg(s)$, Cl^- is therefore a suitable comparison system in the neutralized HCl for which Na/H > 0.5. The proton reduction overpotential is rather weak on gold as well as on platinum while mercury offers the largest potential limit, especially for the highest Na/H ratios. A comparable slight variation in the potential of the different system and then in their activity transfer coefficients is observed when the hydrochloric acid progressively gets neutralized.

Acknowledgment

We would like to express our appreciation to Dr. M. Ndikontar (University of Yaoundé I) for helpful comments.

Literature Cited

(1) Marcus, Y.; Kertes, A. S. *Ion exchange and Solvent Extration of Metal Complex*es; Wiley-Interscience: New York, 1969; p 42.

(2) Fifnides, S.; Largman, T.; Tunick, A. A.; Koff, F. W. *Hydrometallurgy* **1981**, *7*, 201.

(3) (a) Louis, C.; Bessiere, J. Concentrated Phosphoric Acid Media: Acid−Base, Oxidation−Reduction, and Solvation Properties. *J. Chem. Eng. Data* **1986**, *31*, 472−474. (b) Louis, C.; Bessiere, J. Propriétés de solvation des solutions concentrées en acide phosphorique. *Can. J. Chem.* **1986**, *64*, 608−614.

(4) Bessiere, J.; Pillet, Y. Etude des milieux $H_2O-H_2SO_4-HF$ par voie électrochimique. Mesure de l'activité fluorimétrique dans les milieux acides. *Verres Refract.* **1978**, *32*, 24−28.

(5) Slack, A. V. *Phosphoric Acid*; Marcel Dekker Inc.: New York, 1966; Vol 1, Parts 1 and 2.

(6) Bessiere, J.; Aroua, M. K. Détermination par voie électrochimique des propriétés acido-basiques et oxydo-réductrices des solutions concentrées en acide phosphorique progressivement neutralisées par la soude. *Can. J. Chem.* **1992**, *70*, 1843−1848.

(7) Adams, R. N. Carbon paste electrodes. *Anal. Chem.* **1958**, *30*, 1576.

(8) Adams, R. N.; Macoux, L. S.; Pratem, K. B. A non aqueous carbone paste electrode. *Anal. Chem.* **1965**, *37*, 1446−1447.

(9) Ngameni, E.; Tonle, I. K.; Nanseu, C. P.; Wandji, R. Voltammetry study of 2-hydroxy-3-isopropenyl-1,4-naphthoquinone using a carbon paste electrode. *Electroanalysis* **2000**, *12* (11), 847−852.

(10) Strehlow, H. In *The Chemistry of non aqueous solvent*; Lagowski, J. J., Ed.; Academic Press: New York, 1966; Vol. 1, Chapter 4.

(11) Bessiere, J.; Aroua, K.; Louis, C. Prediction of the Acidity Level of Concentrated Mineral Acid Mixtures. *J. Solution Chem.* **1993**, *22*, 243−252.

(12) Bessiere, J.; Aroua, M. K.; Pillet, Y. Détermination directe du niveau d'acidité des solutions concentrées en acide phosphorique progressivement neutralisées, par potentiométrie à intensité imposée. *Analusis* **1991**, *19*, 355−358.

(13) Babale, D. D.; Wandji, R.; Bessiere, J. Concentrated Hydrochloric Acid Media: Acid−Base, Oxidation−Reduction, and Solvatation Properties. *J. Chem. Eng. Data* **1990**, *35*, 345−347.

(14) Lucas, M. Thèse de Doctorat, Paris (France), 1970.

(15) Sella, C. Thèse de Doctorat, Paris VI (France), 1989.

(16) Bates, R. G. *Electrometric pH Determinations*; J. Wiley & Sons, Inc.: New York, 1954.

(17) Majima, H.; Awakura, Y.; Takeshima, V.; Sato, K. Determination of water activities in aqueous solutions of hydrochloric acid-metal chloride. *Denki Kagaku* **1984**, *52*, 800−806.

(18) Ngameni, E.; Bodio, B.; Wandji, R.; Bessiere, J. Redox Potentials in Ammonium Nitrates Solutions. *J. Chem. Eng. Data* **1995**, *40*, 435−437.

Received for review February 17, 2003. Accepted May 15, 2003.

JE0301343