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Concentrated Phosphoric Acid Solutions Neutralized by Sodium Hydroxide: Acid–Base, Oxidation–Reduction, and Solvation Properties

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Phosphoric acid solutions progressively neutralized by sodium hydroxide are characterized by means of the R_0(H) (−log a_{H^+}) acidity function and the $R_0(H_2PO_4^-)$ (−log $a_{H_2PO_4^-}$), $R_0(HPO_4^{2-})$ (−log $a_{HPO_4^{2-}}$) and $R_0(PO_4^{3-})$ (−log $a_{PO_4^{3-}}$) functions which represent the aptitude of these solutions to liberate the protons and the $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} species, respectively. Their solvation properties are characterized by means of the solvation-transfer activity coefficients of the solutes which are calculated from the measured emf of the corresponding redox systems. The behavior of the water activity during the neutralization of 5.5 mol/L phosphoric acid is studied.

Introduction

Phosphoric acid solutions produced in the industrial processing of phosphate ores are about 5.5 and 11.5 mol/L (30% and 50% P_2O_5). They contain valuable species such as uranium in the presence of iron, sulfate, and fluoride (hexafluorosilicate) at fairly high concentrations of phosphoric acid (*1–6*) and toxic elements such as cadmium and arsenic which must be eliminated if the product is to be used in the food industry (*7–9*).

The improvement of the successive stages in the industrial process is possible if the thermodynamic properties such as the activity of water and solvation properties are known (*10–12*).

In this paper, the results of an electrochemical study of 5.5 mol/L solutions of H_3PO_4 progressively neutralized by sodium hydroxide are presented and used to determine the evolution of species (metals and other particules) reactivity during neutralization. The R_0(H) acidity function and the $R_0(H_2PO_4^-)$, $R_0(HPO_4^{2-})$, and $R_0(PO_4^{3-})$ functions characterizing phosphate anion activities and solvatation-transfer coefficients of solutes which are significant in the hydrometallurgy field and corrosion have been determined. Along with water activity results they allow an explanation of the change of oxidation–reduction, precipitation reactions, and extraction processes with acid concentration. Indeed the expressions giving constants of extraction, precipitation, etc. of reactions depend only on R_0(H), $R_0(H_2PO_4^-)$, $R_0(HPO_4^{2-})$, $R_0(PO_4^{3-})$, solvation-transfer activity coefficients, and the activity of water. In a succeeding paper a number of reactions will be studied.

The original solution which is progressively neutralized by sodium hydroxide is H_3PO_4 (5.5 mol/L), and NaOH is introduced progressively in solutions. For example, when 2.0 mol/L of NaOH is added to the original solution, 2.0 mol/L NaH_2PO_4 is formed and 3.5 mol/L H_3PO_4 remains in solution. By convention the notation used is 3.5 mol/L. If 6.0 mol/L of NaOH is added to the original solution, 5.0 mol/L of NaH_2PO_4 and 0.5 mol/L Na_2HPO_4 are formed and there is no H_3PO_4 in the final solution. By convention the notation used is (−0.5 mol/L), (0.5 mol/L is the concentration of Na_2HPO_4). Na/P represents the ratio of NaOH added to the total phosphate concentration ([total phosphate] = 5.5 mol/L).

Table 1. Composition of Neutralized Phosphoric Acid Solutions: Writing Convention

$[H_3PO_4]_{rest}$ (mol/L)	$[NaOH]_{added}$ (mol/L)	Na*/P[a]	$[NaH_2PO_4]_{formed}$ (mol/L)	$[Na_2HPO_4]_{formed}$ (mol/L)
5.5	0.0	0.0	0.0	0.0
5.0	0.5	0.09	0.5	0.0
4.5	1.0	0.18	1.0	0.0
4.0	1.5	0.27	1.5	0.0
3.5	2.0	0.36	2.0	0.0
3.0	2.5	0.45	2.5	0.0
2.0	3.5	0.63	3.5	0.0
1.0	4.5	0.81	4.5	0.0
0.5	5.0	0.90	5.0	0.0
0.0	5.5	1.00	5.5	0.0
−0.5	6.0	1.09	5.0	0.5

[a] Na*/P = [NaOH] (mol/L)/[total phosphate] (mol/L) = [NaOH] (mol/L)/5.5 mol/L.

Results

1. ***R_0(H) Acidity Function*** **(*13–18*).** The R_0(H) acidity function is determined from the variation with the acid concentration of *o*-chloranil/*o*-hydrochloranil ($oQ_s/oQH_{2(s)}$) redox system potentials ($E^a_{oQs/oQH_{2(s)}}$) referred to the ferricinium/ferrocene (Fc^+/Fc) comparison system (Table 3) according to the relations

$$R_0(H) = (E^w oQ_s/oQH_{2(s)} - E^a oQ_s/oQH_{2(s)})/0.058 \quad (1)$$

$$E^w oQ_s/oQH_{w(s)} = 0.453 \text{ V vs } Fc^+/Fc$$

(The superscript a corresponds to the acid medium (neutralized or not) and the superscript w to water).

1.1. o-Chloranil/o-Hydrochloranil (oQ_s/oQH_{2s}). Zero current potentiometry at the carbon paste electrode (acetylene black) containing the *o*-chloranil (oQ_s, $C_6Cl_4O_2$) as the electroactive substance was used for the determination of *o*-chloranil/*o*-hydrochloranil ($oQ_s/oQH_{2(s)}$) system redox potentials ($E_{oQ_s/oQH_{2(s)}}$). The potential values (mV vs Fc^+/Fc) are given in Table 2. The potential values of the $H^+/H_{2(g)}$ system (Table 2) are calculated from those of $oQ_s/oQH_{2(s)}$ (*19*).

2. $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} Anion Activities **(*16, 18*).** By analogy with the R_0(H) acidity function, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} anion activities are characterized by the $R_0(H_2PO_4^-)$, $R_0(HPO_4^{2-})$, and $R_0(PO_4^{3-})$ functions. $R_0(HPO_4^{2-})$ = −log $a_{HPO_4^{2-}}$ characterizes the aptitude of solutions to liberate HPO_4^{2-} anion. It is determined from the variations with acid

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Table 2. Normal Potentials (±5 mV) of Redox Systems in Phosphoric Acid (5.5 mol/L) Progressively Neutralized by Sodium Hydroxide (Potentials in mV vs Fc^+/Fc)

	$[H_3PO_4]$ (mol/L)											
	H_2O	5.5	5.0	4.5	4.0	3.5	3.0	2.0	1.0	0.5	0.0	−0.5
SCE in H_3PO_4 (0.1 mol/L)	−158	40	25	0	−10	−30	−40	−65	−120	−130	−135	−140
$oQ_s/oQH_{2(s)}$	611	562	547	522	511	486	470	429	349	326	264	232
$H^+/H_{2(g)}$	−400	−290	−305	−330	−341	−366	−382	−423	−503	−526	−588	−620
Cu^{2+}/Cu	−60	0	−15	−25	−35	−45	−55	−75	−125	−155	−175	−195
Cd^{2+}/Cd	−755	−600	−610	−620	−635	−645	−660	−700	−745	−760	−770	−780
Zn^{2+}/Zn	−1140	−1000	−1015	−1020	−1035	−1040	−1055	−1075	−1120	−1130	−1145	
Sn^{2+}/Sn	−530	−510	−525	−550	−560	−565	−575	−600	−680	−700	−725	−775
Pb^{2+}/Pb	−520	420	−425	−430	−440	−450	−460	−490	−525	−565	−590	−605
Fe^{3+}/Fe^{2+}	370	150	135	110	85	50	30	−25	−105	−125	−190	−250
UO_2^{2+}/U^{4+}	−66	232	176	160	95		13					
Ag^+/Ag	400	495	494	492	483	472	461	432	379	365	350	330
$AgCl/Ag$	−178	−83	−90	−99	−102	−106	−109	−138	−180	−187	−196	−204
$AgBr/Ag$	−329	−245	−247	−249	−253	−255	−260	−277	−332	−334	−338	−340
AgI/Ag	−520	−450	−450	−453	−455	−470	−483	−510	−540	−545	−547	−551
AgLET/Ag	−203	−60	−79	−107	−120	−152	−163	−195	−248	−251	−259	−271
$Hg_2HPO_{4(s)}/Hg_s$	24	380	365	344	334	314	300	273	220	200	145	132
$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$	−40	510	469	411	382	348	323	270	191	177	165	154

Table 3. R_0(H), $R_0(H_2PO_4^-)$, $R_0(HPO_4^{2-})$, $R_0(PO_4^{3-})$ (±0.1), and log a_{H_2O}[a]

$[H_3PO_4]$ (mol/L)	R_0(H)	$R_0(H_2PO_4^-)$	$R_0(HPO_4^{2-})$	$R_0(PO_4^{3-})$	log a_{H_2O}[a]
5.5	−1.9	4.8	13.9	28.2	−0.10
5.0	−1.7	4.5	13.4	27.5	
4.5	−1.2	4.3	12.7	26.3	
4.0	−1.1	4.0	12.3	25.8	−0.12
3.5	−0.6	3.9	11.7	24.7	
3.0	−0.3	3.7	11.2	23.9	
2.0	0.4	3.4	10.2	22.2	
1.0	1.7	2.9	8.4	19.1	
0.5	2.1	2.6	7.7	18.0	
0.0	3.2	1.8	5.8	15.0	−0.13
−0.5	3.8	2.0	5.4	14.0	

[a] a_{H_2O} is determined at 20 °C by means of isopiestic measurements.

concentration of the *E* redox potentials of $Hg_2HPO_{4(s)}/Hg_s$ system involving HPO_4^{2-} as the only soluble species (Table 3) according to the relation

$$R_0(HPO_4^{2-}) = 2(E^a_{Hg_2HPO_{4(s)}/Hg_s} - E^w_{Hg_2HPO_{4(s)}/Hg_s})/0.058 \tag{2}$$

$$E^w_{Hg_2HPO_{4(s)}/Hg_s} = -0.024 \text{ V vs } Fc^+/Fc$$

The superscript a corresponds to the acid medium (neutralized or not) and the superscript w to water.

2.1. ***$Hg_2HPO_{4(s)}/Hg_s$ System.*** Zero current potentiometry at the carbon paste electrode (acetylene black) containing mercury phosphate ($Hg_2HPO_{4(s)}$) (prepared in the laboratory (*19*) was used for the determination of the $Hg_2HPO_{4(s)}/Hg_s$ system redox potentials ($E_{Hg_2HPO_{4(s)}/Hg_s}$). The potential values are given in Table 2 and are used to calculate the $R_0(HPO_4^{2-})$ function (relation 2).

$R_0(H_2PO_4^-)$ and $R_0(PO_4^{3-})$ are calculated according to the relations

$$pK_2 = 7.2 = R_0(H) + R_0(HPO_4^{2-}) - R_0(H_2PO_4^-) \tag{3}$$

$$pK_3 = 12.4 = R_0(H) + R_0(PO_4^{3-}) - R_0(HPO_4^{2-}) \tag{4}$$

The results are given in Table 3.

3. ***Variations of Solute Solvation.*** They are characterized by means of their solvation-transfer activity coefficients. The log *f* coefficients are calculated from normal potential values of the corresponding redox systems (Table 2) according to relations 5–8.

By convention, the notation M^{n+} is used in all cases, irrespective of the exact form of the species. $M^{n+} = \Sigma M^{n+}$ solvated. Indeed M^{n+} can be solvated by solvent species or/and molecules of water. $f > 1$ (or $\log f > 0$) signifies that the species is less solvated in the solution under study than in water; $f < 1$ (or $\log f < 0$) signifies that the species is more solvated in the solution than in water.

M^{n+}/Ms system

$$\log f_{M^{n+}} = n(E_0^a - E_0^w)/0.058 \tag{5}$$

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

$$\log f_{M^{n+}}/f_{M^{(n-m)+}} = m(E_0^a - E_0^w)/0.058 \tag{6}$$

$MO_p^{n+}/MO_q^{(n+2(p-q)-m)+}$ system

$$\log f_{MO_p^{n+}}/f_{MO_q^{(n-2(p-q)-m)+}} = m(E_0^a - E_0^w)/0.058 + 2(p-q)R_0(H) + (p-q)\log a_{H_2O} \tag{7}$$

AX_n/A_s system

$$\log f_{X^-} = n(E_0^w - E_0^a)/0.058 \tag{8}$$

E_0^w represents the normal potential of the considered redox system in water and E_0^a its value (referred to Fc^+/Fc) in a phosphoric medium (neutralized or not) characterized by its acidity level R_0(H) and its water activity a_{H_2O}.

$MHPO_{4(s)}$ phosphate

$$\log f_{M^{2+}} = R_0(HPO_4^{2-}) - pK_s^w - \log [M^{2+}] \tag{9}$$

$R_0(HPO_4^{2-})$ characterizes the ability of the phosphoric medium to give HPO_4^{2-} species, and pK_s^w represents the $MHPO_4$ solubility product in water. The results are given in Table 4.

Normal potential values of the considered redox systems were determined directly by means of classical electrochemical methods: pulse polarography, dc polarography, zero current potentiometry, amperometry (Table 2).

The polarography was used for: Cu^{2+}/Cu (Hg), Cd^{2+}/Cd (Hg), Zn^{2+}/Zn (Hg), Sn^{2+}/Sn (Hg), Pb^{2+}/Pb (Hg), and Fe^{3+}/Fe^{2+}.

In the case of rapid systems, normal potentials and half-wave potentials are considered as equal while the diffusion coefficients of cations in solution and in the amalgam are the

Table 4. Solvation Activity Coefficients in Phosphoric Acid Solutions Progressively Neutralized by Sodium Hydroxide

	$[H_3PO_4]$ (mol/L)										
	5.5	5.0	4.5	4.0	3.5	3.0	2.0	1.0	0.5	0.0	−0.5
$\log f_{Ag^+}$	1.6	1.6	1.6	1.4	1.2	1.1	0.6	0.4	−0.6	−0.9	−1.2
$\log f_{Cu^{2+}}$	2.0	1.6	1.2	0.9	0.6	0.2	−0.5	−2.2	−3.2	−3.9	−4.6
$\log f_{Cd^{2+}}$	5.3	5.0	4.7	4.1	3.8	3.3	1.9	0.3	−0.2	−0.5	−0.9
$\log f_{Zn^{2+}}$	4.8	4.3	4.1	3.6	3.4	2.9	2.2	0.7	0.3	−0.1	
$\log f_{Sn^{2+}}$	0.7	0.2	−0.7	−1.0	−1.2	−1.6	−2.4	−5.1	−5.9	−6.9	−8.4
$\log f_{Pb^{2+}}$	3.4	3.3	3.1	2.8	2.4	2.1	1.0	−0.2	−1.6	−2.4	−2.9
$\log f_{Fe^{3+}}/f_{Fe^{2+}}$	−3.8	−4.1	−4.5	−4.9	−5.5	−5.9	−6.8	−8.2	−8.5	−9.7	−10
$\log f_{Fe(CN)_6^{3-}}/f_{Fe(CN)_6^{4-}}$	9.5	8.8	7.8	7.3	6.7	6.3	5.3	4.0	3.7	3.5	3.3
$\log f_{UO_2^{2+}}/f_{U^{4+}}$	2.5	1.3	1.2	0.9		0.4					
$\log f_{Cl^-}$	−1.6	−1.5	−1.4	−1.3	−1.2	−1.2	0.7	0.0	0.2	0.3	0.4
$\log f_{Br^-}$	−1.4	−1.4	−1.4	−1.3	−1.3	−1.2	−0.9	0.1	0.1	0.2	0.2
$\log f_{I^-}$	−1.2	−1.2	−1.1	−1.1	−0.8	−0.6	−0.2	0.3	0.4	0.5	0.5
$\log f_{LET^-}$	−2.4	−2.1	−1.7	−1.4	−0.9	−0.7	−0.1	0.8	0.9	1.0	1.2

same. In concentrated phosphoric media, diffusion coefficient variations are determined and the correction is considered.

Standard potentials are determined by potentiometry at a silver electrode for Ag^+/Ag, AgCl/Ag, AgBr/Ag, AgI/Ag, and AgLET/Ag (LET = diethyl dithiophosphate) and at a platinum electrode for $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$.

In the case of uranium, normal potential values are calculated from equilibrium constants of the reaction

$$U(VI) + 2Fe(II) \Leftrightarrow U(IV) + 2Fe(III)$$

These equilibrium contants are calculated from amperometry measurements. In all cases, potential values were measured at room temperature in comparison with the reference electrode: aqueous SCE in a separate compartment containing 0.1 mol/L H_3PO_4.

The determination of water activity was carried out by using the perspiration isopiestic method.

Discussion

The $R_0(H)$ acidity function in neutralized phosphoric acid media (+5.5 to −0.5 mol/L) ranges about six units (−1.9 to +3.8). This variation is more important than in $H_2O-H_3PO_4$ solutions (*10*, *18*, *16*).

It is important to mention that the variation of water activity with acid concentration is insignificant. Then the ion reactivity depends on interaction solvent–ions (neutralized $H_2O-H_3PO_4$ solutes). We concluded also that the $R_0(H)$ values in mixtures of $H_2O-H_3PO_4$ are not equal for the same activity of water; then the law (*20–23*) which was shown for acid solutions (weak and/or strong) is not suitable in this case.

In neutralized phosphoric acid, cations are characterized by the decrease of values of log *f* with the decrease of acid concentration: they are then more and more solvated. For H_3PO_4 concentrations of less than 0.5 mol/L all cations are characterized by negative log *f*; they are then more solvated and less reactive than in water. At the same acidity level, log *f* values increase with the number of cationic charges. At the same acidity level and for the same number of charge, the less stable the corresponding phosphate in water, the higher the log *f* value.

Inversely anions are less and less solvated with decreasing phosphoric acid concentration. For H_3PO_4 concentrations of less than 1.0 mol/L, all anions are less solvated in phosphoric media than in water: the log *f* values are positive. The amplitude of variation of log *f* for anions with phosphoric acid concentration depends on its basic properties. These results allow the prevision of the flotation of cadmium by diethyl dithiophosphate, the acid attack of metals, the solubility of phosphates, and the evolution of equilibrium constants of liquid–liquid extraction reactions (*19*).

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