Table IV. Maximum Errors in Density for the Cross-Square Mixtures Obtained by Using the Equations of Wood and Reilly (*11*)

mixture	$10^6\delta\rho$, g cm^{-3}	
	without ΔV_m	with ΔV_m
NaCl + K_2SO_4	238	72
KCl + Na_2SO_4	171	90

in the presence of the common anion X and the anions X + Y in the presence of the common cation M. This equation attempts to account for cation-cation and anion-anion interactions and neglects higher order triplicate interactions (*11*).

A summary of the maximum errors in density obtained by using the estimate Φ_v (eq 8) and

$$\rho = (10^3 + Me_T)/(e_T\Phi_v + 10^3/\rho_0) \qquad (10)$$

are given in Table IV ($M = \sum E_iM_i$ is the mean equivalent weight of the mixture). The use of the volume of mixing term reduces the maximum errors by 2-3 times compared to use of Young's (*12*) simple additive rule (the first term in eq 8). The maximum errors (90×10^{-6} g cm^{-3}) are still higher than the maximum errors (12×10^{-6} g cm^{-3}) obtained for the original solutions and the full ΔV_m equation but demonstrate the utility of the equation of Wood and Reilly (*11*) for solutions of known composition formed by unknown natural processes.

Registry No. KCl, 7447-40-7; NaCl, 7647-14-5; K_2SO_4, 7778-80-5; Na_2SO_4, 7757-82-6.

Literature Cited

(1) Millero, F. J.; Connaughton, L. M.; Vinokurova, F.; Chetirkin, P. V. *J. Solution Chem.* **1985**, *14*(12), 837-851.
(2) Millero, F. J.; Lampreia, M. *J. Solution Chem.* **1985**, *14*(12), 853-864.
(3) Millero, F. J. *Pure Appl. Chem.* **1985**, *57*, 1015.
(4) Picker, P.; Tremblay, E.; Jolicoeur, J. *J. Solution Chem.* **1974**, *3*, 377.
(5) Kell, G. S. *J. Chem. Eng. Data* **1975**, *20*, 97.
(6) Millero, F. J.; Poisson, A. *Deep-Sea Res.* **1981**, *28*, 625.
(7) Millero, F. J. In *Activity Coefficients in Electrolyte Solutions*; Pytkowicz, R. M., Ed.; CRC Press: Boca Raton, FL 1979; pp 63-151.
(8) Millero, F. J.; Sotolongo, S. University of Miami, Miami, FL, unpublished results, 1983.
(9) Anderson, H. L.; Wood, R. H. In *Water*; Franks, F., Ed.; Plenum: New York, 1973; Vol. III, Chapter 2.
(10) Friedman, H. L. *Ionic Solution Theory*; Wiley-Interscience: New York, 1962; Vol. 3, p 265.
(11) Wood, R. H.; Reilly, P. J. *Annu. Rev. Phys. Chem.* **1970**, *21*, 387.
(12) Young, T. F. *Rec. Chem. Prog.* **1951**, *12*, 81.

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Concentrated Phosphoric Acid Media: Acid-Base, Oxidation-Reduction, and Solvation Properties

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H_2O-H_3PO_4 media (1-14 mol/L) are characterized by means of 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 which represent their ability to give up the proton and the $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} particles, respectively. Their solvation properties 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 systems or from solubility product values. The significance of the parameter water activity is underlined.

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 essentially) at fairly high concentrations (*1*) and others such as cadmium and arsenic which must be eliminated.

Provisions for improving the successive stages in the industrial processes are possible from a thermodynamical point of view by using such data as acidity level, phosphate anion activities, water activity, and solvation properties. The data concerning concentrated phosphoric media existing in the literature nevertheless do not allow us to describe thoroughly their properties: studies dealing with a limited acid concentration range or carried out under peculiar conditions (e.g., in the presence of sulfate) give unreliable results because of incompletely defined reference systems. We present in this paper the results of a study by electrochemical methods of H_2O-H_3PO_4 media (1-14 mol/L) giving the R_0(H) acidity function (*2*), and the $R_0(H_2PO_4^-)$, $R_0(HPO_4^{2-})$, and $R_0(PO_4^{3-})$ functions (*3*, *4*) characterizing phosphate anion activities and solvation transfer coefficients of solutes (*2-4*) especially those which are significant in the hydrometallurgy field. Along with water activities they allow us to explain the changes with acid concentration of oxidation-reduction, precipitation reactions, and extraction processes.

Results

1. R_0(H) Acidity Function. The R_0(H) acidity function (*2-4*) is determined from the variation with the acid concentration of the H^+/H_2 (hydrogen electrode) and the 1,4-benzoquinone/hydroquinone (Q/QH_2) redox system potentials ($E^a_{H^+/H_2}$ and E^a_{Qs/QH_2s}, respectively) referred to the ferrocenium/ferrocene (Fc^+/Fc) comparison system (Table I) according to the relations

$$R_0(H) = (E_0{}^w{}_{H^+/H_2} - E^a{}_{H^+/H_2})/0.058 \qquad \text{with } E_0{}^w{}_{H^+/H_2} = -0.400 \text{ V vs. } Fc^+/Fc \qquad (1)$$

$$R_0(H) = (E^w{}_{Qs/QH_2s} - E^a{}_{Qs/QH_2s})/0.058 \qquad \text{with } E^w{}_{Qs/QH_2s} = +0.316 \text{ V vs. } Fc^+/Fc \qquad (2)$$

(The superscript a corresponds to the acidic medium and the superscript w to water.)

2. $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} Anion Activities. By analogy with the R_0(H) acidity function, $H_2PO_4^-$, HPO_4^{2-}, 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. $R_0(HPO_4^{2-}) = -\log a_{HPO_4^{2-}}$ and R_0-

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Table I. Normal Potentials[a] (±5 mV) of Redox Systems in Phosphoric Media (2–14 mol/L)

	H_3PO_4, mol/L; H_3PO_4, %; P_2O_5, %				
	2.0; 18.0; 13.0	5.5; 42.5; 30.8	8.0; 56.9; 40.9	11.5; 72.5; 52.7	14.0; 83.0; 60.0
Fc^+/Fc	+50	−40	−115	−265	−380
H^+/H_2	−337	−330	−320	−305	−260
Zn^{2+}/Zn	−1050	−1040	−1045	−1050	−1030
V^{3+}/V^{2+}	−700			−865	
Cd^{2+}/Cd	−650	−640	−645	−650	−630
Sn^{2+}/Sn	−500	−490	−480	−450	−430
Pb^{2+}/Pb	−430	−460	−470	−500	−510
AgI/Ag	−420	−480	−530	−600	−680
$AgBr/Ag$	−320	−330	−360	−380	−420
$AgCl/Ag$	−70	−120	−160	−235	−275
$BiPO_4/Bi$	−110	−110	−120	−130	−160
Cu^{2+}/Cu	−20	−40	−50	−65	−80
Fe^{3+}/Fe^{2+}	+170	+109	+75	+29	−20
UO_2^{2+}/U^{4+}	+140	+194	+242	+351	+326
VO^{2+}/V^{3+}	+120	+180	+230	+320	+420
Hg_2HPO_{4s}/Hg_s	+300	+290	+290	+260	+240
Q/QH_2	+378	+360	+345	+345	+340
Q_s/QH_{2s}	+370	+380	+385	+390	+400
Ag^+/Ag	+490	+455	+435	+415	+395
VO_2^+/VO^{2+}	+750	+800	+815	+855	+900
$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$	+380	+460	+535	+665	+850

[a] In mV vs. SCE in 0.1 mol/L H_3PO_4 (*3*).

$(PO_4^{3-}) = -\log a_{PO_4^{3-}}$ are determined from the variations with acid concentration of the E' and E'' redox potentials of Hg_2HPO_{4s}/Hg_s and $BiPO_{4s}/Bi_s$ systems involving HPO_4^{2-} and PO_4^{3-}, respectively, as the only soluble species (Table I) according to the relations

$$R_0(HPO_4^{2-}) = 2(E'^{a} - E'^{w})/0.058 \quad \text{with } E'^{w} = -0.024 \text{ V vs. } Fc^+/Fc \tag{3}$$

$$R_0(PO_4^{3-}) = 3(E''^{a} - E''^{w})/0.058 \quad \text{with } E''^{w} = -0.593 \text{ V vs. } Fc^+/Fc \tag{4}$$

$R_0(H_2PO_4^-)$ is calculated according to the relation

$$pK_2 = 7.2 = R_0(H) + R_0(HPO_4^{2-}) - R_0(H_2PO_4^-) \tag{5}$$

The results are given in Table II.

3. Variations of Solute Solvation. They are characterized by means of their solvation-transfer activity coefficients. The f coefficients are calculated from normal potential values of the corresponding redox systems (Table I) according to the relations 6–9 or from solubility product values according to the relations 10 and 11.

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

$$M^{n+}/M^{(n-m)+} \text{ system} \quad \log f_{M^{n+}}/f_{M^{(n-m)+}} = m(E_0^{a} - E_0^{w})/0.058 \tag{7}$$

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

$$\log f_{MO_p^{n+}}/f_{MO_q^{[n+2(p-q)-m]+}} = m(E_0^{a} - E_0^{w})/0.058 + 2(p-q)R_0(H) + (p-q)\log a_{H_2O} \tag{8}$$

$$AX_n/A_s \text{ system} \quad \log f_{X^-} = (E_0^{w} - E_0^{a})/0.058 \tag{9}$$

E_0^{w} represents the normal potential of the considered redox system in water, E_0^{a} its value (referred to Fc^+/Fc) in a phosphoric medium characterized by its acidity level $R_0(H)$ and its water activity a_{H_2O}.

$$MX \text{ compound} \quad pK_s^{a} - pK_s^{w} = \log f_{M^+} \log f_{X^-} \tag{10}$$

pK_s^{a} represents the solubility product of the MX compound in the phosphoric medium and pK_s^{w} its value in water.

$$XHPO_4 \text{ phosphate} \quad \log f_{X^{2+}} = R_0(HPO_4^{2-}) - pK_s^{w} - \log [X^{2+}] \tag{11}$$

$R_0(HPO_4^{2-})$ characterizes the ability of the phosphoric medium to give HPO_4^{2-} species and pK_s^{w} represents $XHPO_4$ solubility product in water. The results are given in the Table III.

Normal potential values of the considered redox systems were determined directly by means of classical electrochemical methods (*3*), (a) dc polarography, (b) zero-current potentiometry, and (c) voltamperometry at rotating disk electrodes (smoothed platinum, vitreous carbon). (a) In the case of rapid system, normal potentials and half-wave potentials are considered as equal while the diffusion coefficients of cations in solution and in amalgam are the same. In concentrated phosphoric media, diffusion coefficient variations were determined and the correction calculated which is significant in phosphoric media more concentrated than 8 mol/L. (b) Normal potentials were determined from Nernst law verification. (c) In the case of uranium, normal potential values were calculated from equilibrium constants of the reactions

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

in phosphoric media less concentrated than 6 mol/L and

$$U(VI) + 2Ag(0) \rightleftarrows U(IV) + 2Ag(I)$$

in concentrated phosphoric media. These equilibrium constants were calculated from vis-spectrophotometric and/or potentiometric measurements. In all cases, potential values were measured at 20 °C in comparison with the following reference electrode: aqueous SCE in a separate compartment containing 0.1 mol/L H_3PO_4.

Table II. $R_0(H)$, $R_0(H_2PO_4^-)$, $R_0(HPO_4^{2-})$, $R_0(PO_4^{3-})$ (±0.1), $\log a_{H_2O}$ (*23, 24*), and $\log a_{H_3PO_4}$ (*23, 24*)

H_3PO_4, mol/L	$R_0(H)$		$R_0(H_2PO_4^-)$	$R_0(HPO_4^{2-})$	$R_0(PO_4^{3-})$	$\log a_{H_2O}$	$\log a_{H_3PO_4}$
	H^+/H_2	Q/QH_2					
1	+0.2	+0.4	+1.7	+8.4	+20.8	−0.009	0
2	−0.2	−0.1	+2.2	+9.4	+22.4	−0.021	+0.43
3	−0.7	−0.5	+2.5	+10.1	+23.7	−0.036	+0.72
4	−1.1	−1.0	+2.8	+11.0	+25.0	−0.057	+1.0
5	−1.7	−1.5	+2.9	+11.8	+26.0	−0.084	+1.25
5.5	−1.9	−1.8	+3.3	+12.2	+26.8	−0.100	+1.38
6	−2.1	−2.0	+3.5	+12.7	+27.3	−0.119	+1.50
7	−2.7	−2.7	+3.8	+13.7	+28.8	−0.162	+1.76
8	−3.2	−3.2	+4.3	+14.8	+30.4	−0.217	+2.05
9	−3.9	−4.0	+4.7	+15.9	+32.2	−0.285	+2.30
10	−4.7	−4.7	+5.0	+17.0	+34.3	−0.371	+2.58
11	−5.6	−5.4	+5.3	+18.2	+36.3	−0.47	+2.80
11.5	−6.1	−5.9	+5.6	+18.9	+37.6	−0.52	+2.93
12	−6.7	−6.3	+5.6	+19.4	+38.4	−0.595	+3.04
13	−7.7	−7.0	+5.8	+20.8	+40.2	−0.75	+3.26
14	−8.9	−8.0	+6.0	+22.2	+42.0	−0.92	+3.47

Table III. Solvation-Transfer Activity Coefficients in Phosphoric Acid Media (2-14 mol/L)

	H_3PO_4, mol/L				
	2.0	5.5	8.0	11.5	14.0
$\log f_{Ag^+}$	+0.7	+1.6	+2.6	+4.8	+6.4
$\log f_{Hg^{2+}}$	0.0	+2.2	+4.0	+7.3	+11.0
$\log f_{Pb^{2+}}$	+1.3	+3.4	+5.8	+8.7	+12.7
$\log f_{Cu^{2+}}$	−0.3	+2.0	+4.5	+8.3	+11.6
$\log f_{Sn^{2+}}$	−0.7	+2.7	+5.9	+10.7	+16.5
$\log f_{Cd^{2+}}$	+3.4	+6.9	+9.3	+13.1	+18.2
$\log f_{Zn^{2+}}$	+2.0	+5.5	+7.9	+11.8	+16.8
$\log f_{Fe^{3+}}/f_{Fe^{2+}}$	−4.3	−3.8	−3.1	−1.3	−0.2
$\log f_{V^{3+}}/f_{V^{2+}}$	−1.6			+0.9	
$\log f_{Fe(CN)_6^{3-}}/f_{Fe(CN)_6^{4-}}$	+6.4	+9.3	+11.9	+16.7	+21.9
$\log f_{UO_2^{2+}}/f_{U^{4+}}$	+4.0	+2.5	+1.3	−1.9	−10.8
$\log f_{VO_2^+}/f_{VO^{2+}}$	+1.3	+0.2	−0.9	−3.8	−7.0
$\log f_{VO^{2+}}/f_{V^{3+}}$	+1.9	+1.0	+0.5	−1.8	−3.8
$\log f_{H_3AsO_4}/f_{AsO^+}$	+2.0	−1.4	−3.9		
$\log f_{Cl^-}$	−1.0	−1.6	−2.1	−3.6	−4.9
$\log f_{Br^-}$	+0.7	−0.5	−1.5	−3.4	−4.8
$\log f_{I^-}$	−1.4	−1.9	−2.4	−3.5	−4.3
$\log f_{F^-}$	−3.4	−5.0	−6.1	−8.9	
$\log f_{SO_4^{2-}}$	−3.3	−6.0	−8.5	−11.5	−15.6
$\log f_{Fe(CN)_6^{4-}}$	−8.1	−12.7			
$\log f_{Fe(CN)_6^{3-}}$	−1.7	−3.3			
$\log f_{I_3^-}$	−3.3	−4.0	−5.5		

Discussion

The $R_0(H)$ values calculated from the H^+/H_2 and the Q/QH_2 potential values are very close in the case of H_3PO_4 concentrations less than 11 mol/L. For higher concentrations we considered only the $R_0(H)$ values resulting from H^+/H_2 potential values because of a visible transformation of the 1,4-benzoquinone species. The acidity level in 1–14 mol/L phosphoric acid media ranges over nine units (+0.2 to −8.9); the gap between the acidity level in the 5.5 and 11.5 mol/L industrial media is about four units. These values are very close to those corresponding to the H_{GF} (*5*, *6*) and H'_R (*7*, *8*) acidity functions but clearly different from those of the H_0 acidity function (*9*, *10*). That could justify afterward the use of the glass electrode as the H^+ indicating electrode in the concentrated phosphoric media and would show that aniline Hammett indicators would be more sensitive to solvation than carbinol indicators leading to H'_R acidity function whose behavior is similar to that of ferrocene.

Bell and Bascombe (*11*) and Wyatt (*12*) showed that for an equal water activity value, strong acid media had an equal H_0 acidity level and that this property did not hold in the case of weak acids especially HF and H_3PO_4, proving that acid anions do not interefere in the solvation variation of Hammett indicators but that water and undissociated acid molecules which are present in weak acid media do. The same comparison carried out using the $R_0(H)$ acidity function in $H_2O-H_2SO_4$ (*13*, *14*), H_2O-HCl (*15*), H_2O-HF (*16*, *17*), and $H_2O-H_3PO_4$ (*2*, *3*) leads to the conclusion that for the same value of water activity (*18–24*), strong and weak acids are characterized by the same $R_0(H)$ acidity level, indicating that the nature of the anion and/or the presence of undissociated acid molecules do not interfere.

As in $H_2O-H_2SO_4$, H_2O-HCl, and H_2O-HF media, cations in $H_2O-H_3PO_4$ media are characterized by positive and increasing with acid concentration log *f* values. They are thus less solvated and more reactive in the more concentrated phosphoric media. 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 charges, the less stable the corresponding phosphate in water, the higher the log *f* value. Anions are characterized by negative and decreasing log *f* values with increasing acidity. They are then more solvated in the more concentrated phosphoric media. For a given acidity level, the higher the number of anion charges and the stronger its basic properties the higher (absolute value) the log *f* value.

Registry No. H_3PO_4, 7664-38-2.

Literature Cited

(1) Habashi, F. *Proc.—2nd Int. Congr. Phosphorus Compd April 1980, Boston* **1980**, 629–660.
(2) Louis, C.; Bessière, J. *Anal. Lett.* **1980**, *13* (A.11), 937–946.
(3) Louis, C. Thèse de Doctorat d'Etat, Nancy, 1983.
(4) Louis, C.; Bessière, J. *Can. J. Chem.* **1985**, *63* (4) 908–916.
(5) Janata, J.; Jansen, G. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 1656–1665.
(6) Modro, T. A.; Yates, K.; Janata, J. *J. Am. Chem. Soc.* **1975**, *97*, 1492–1499.
(7) Arnett, E. M.; Mach, G. W. *J. Am. Chem. Soc.* **1964**, *86*, 2671–2677.
(8) Arnett, E. M.; Mach, G. W. *J. Am. Chem. Soc.* **1966**, *88*, 1177–1183.
(9) Gel'bshtein, A. I.; Shcheglova, G. G.; Temkin, M. I. *J. Inorg. Chem. USSR* **1956**, *1* (2), 282–297.
(10) Heilbronner, E.; Weber, S. *Helv. Chim. Acta* **1949**, *32* (201), 1513–1517.
(11) Bascombe, K. N.; Bell, R. P. *Faraday Discuss. Chem. Soc.* **1957**, *24*, 158–161.
(12) Wyatt, P. A. H. *Faraday Discuss. Chem. Soc.* **1957**, *24*, 162–170.
(13) Bouchet, M. Thèse de Doctorat d'Etat, Paris, 1973.
(14) Bauer, D.; Bouchet, M. *C. R. Acad. Sc., Sér. C.* **1972**, *275* (1), 21–24.
(15) Babale, D. D. Thèse de Doctorat de 3° Cycle. Yaounde, 1981.
(16) Vaillant, A. Thèse de Doctorat de 3° Cycle. Paris, 1974.
(17) Vaillant, A.; Devynck, J.; Tremillon, B. *Anal. Lett.* **1973**, *6* (12), 1095–1099.
(18) Bell, R. P.; Bascombe, K. N.; McCoubrey, J. C. *J. Chem. Soc.* **1956**, 1286–1291.
(19) Hyman, H. H.; Kilpatrick, M.; Katz, J. J. *J. Am. Chem. Soc.* **1957**, *79*, 3668–3671.
(20) Simons, J. H. *Fluorine Chemistry*; Simons, J. H., Ed.; Academic: New York, 1950; Vol. 1, p 225.
(21) Randall, M.; Young, L. E. *J. Am. Chem. Soc.* **1928**, *50*, 989–1004.
(22) Giauque, W. F.; Hornung, E. W.; Kunzler, J. E.; Rubin, T. R. *J. Am. Chem. Soc.* **1960**, *82*, 62–70.
(23) Elmore, K. L.; Masson, C. M.; Christensen, J. H. *J. Am. Chem. Soc.* **1946**, *68*, 2528–2532.
(24) Elmore, K. L.; Hatfield, J. D.; Dunn, R. L.; Jones, A. D. *J. Phys. Chem.* **1965**, *69*, 3520–3525.

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