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Solubility of Magnesium Hydrogen Phosphate Trihydrate and Ion-Pair Formation in the System $Mg(OH)_2$–H_3PO_4–H_2O at 25 °C

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The solubility of $MgHPO_4{\cdot}3H_2O$ is determined in the ternary system $Mg(OH)_2$–H_3PO_4–H_2O at 25 °C in the range $5.0 < pH < 7.3$. The solubility behavior can consistently be described by taking into account the formation of the ion pairs of $MgH_2PO_4^+$ and $MgHPO_4$. The thermodynamic solubility product of $MgHPO_4{\cdot}3H_2O$ and the thermodynamic association constants for $MgH_2PO_4^+$ and $MgHPO_4$ with their standard error are determined as $(1.67 \pm 0.03) \times 10^{-6}$ mol^2/L^2, $(1.89 \pm 0.17) \times 10$ M^{-1}, and $(7.12 \pm 0.23) \times 10^2$ M^{-1}, respectively.

Introduction

Magnesium hydrogen phosphate trihydrate (hereafter referred to as MHPT), $MgHPO_4{\cdot}3H_2O$, is found as the mineral newberyite and as a constituent of human and animal calculi.[2] Knowledge of its solubility behavior is pertinent to the study of the formation and stability of this phosphate whether mineral or biological.[3]

Only two values are reported in the literature for the thermodynamic solubility product of MHPT at 25 °C.[4,5] They were calculated on the assumption that only Mg^{2+} and HPO_4^{2-} ions form ion pairs. However, the values for the thermodynamic association constant for the $MgHPO_4$ ion pair reported in the literature are not in good agreement.[5–7] Moreover, there are indications that Mg^{2+} and $H_2PO_4^-$ also form ion pairs to a significant extent.[8–10] Apart from a few values for the apparent association constant for the $MgH_2PO_4^+$ ion pair, which vary with the experimental conditions used,[9–12] no value for the thermodynamic constant is reported.

Since the value of the thermodynamic solubility product of MHPT depends on the values of the ion-pair association constants used, the solubility of MHPT was determined in the dilute range of the system $Mg(OH)_2$–H_3PO_4–H_2O at 25 °C in the pH range 5.0–7.3. From the solubility data the thermodynamic solubility product of MHPT and the thermodynamic association constants of $MgH_2PO_4^+$ and $MgHPO_4$ were estimated by using a generalized least-squares procedure. Equilibrations were made in the ternary system to avoid complications in the interpretation of data that might result from the presence of other ions.

Experimental Section

Chemicals. For the preparation of solutions and samples analytical reagent grade chemicals were used throughout. Only water freshly generated by a Milli-Q system (Millipore) and kept free of CO_2 was used.

MHPT was prepared by using a slight modification of the method described by Taylor et al.[5] The pH of the magnesium- and phosphate-containing solution was adjusted to 4 by the addition of acetic acid, and MHPT was precipitated at 40 °C. The precipitate was left in contact with the mother liquor overnight at 40 °C and then for 1 day at room temperature. The solid was filtered off, washed repeatedly with small quantities of water, and dried at 60 °C. The precipitate consisted of homogeneous crystals containing 13.97 ± 0.03 wt % Mg, 17.81 ± 0.04 wt % P, and 36.14 ± 0.04 wt % H_2O (theoretical: 13.95, 17.77, and 36.17 wt %, respectively). The X-ray diffraction pattern and the IR spectrum showed sharp and well-resolved peaks, indicating a good crystallinity. All peaks in the diffraction pattern could be indexed on the basis of the orthorhombic space group *Pbca* of $MgHPO_4{\cdot}3H_2O$.[2a,13] The lattice parameters were determined from the position of 36 reflections in the X-ray diffraction pattern obtained in a Philips Guinier camera (Type XDL 700) using Cu Kα radiation and α-Al_2O_3 as an internal standard. The parameters $a = 10.204 \pm 0.004$ Å, $b = 10.675 \pm 0.004$ Å, and $c = 10.008 \pm 0.007$ Å agree with those reported by Abbona et al.[13]

Phosphoric acid solutions used in the equilibrations were prepared from a H_3PO_4 stock solution. The concentration of these dilute solutions was checked regularly, and the uncertainty in the concentration was estimated as 0.5%.

Equilibrations. Weighed amounts of MHPT were added to 250 mL of phosphoric acid solution in 500-mL polyethylene flasks. The flasks were slowly rotated end-over-end in a water bath at 25.00 ± 0.02 °C. Preliminary equilibrations, lasting up to 21 days, showed that the solution attained a constant composition within experimental error after 2–3 days' equilibration. Therefore, in all subsequent experiments the samples were equilibrated for at least 10 days. After equilibration, the suspensions were filtered through Millipore filters (0.22-μm pore size). Samples of the clear filtered solutions were taken for pH measurement and for determination of magnesium and phosphorus.

During all manipulations care was taken to avoid contamination of the solutions with atmospheric CO_2.

Analyses. The magnesium content of solutions containing 10^{-2} M Mg or more was determined by titration with EDTA after separation of the phosphate by means of an anion exchanger in the chloride form. The uncertainty in the amount analyzed was determined as 0.3%. In less concentrated solutions, magnesium was determined by atomic absorption spectrometry. Lanthanum was added to samples and standards to suppress interference by phosphate. In that case the uncertainty was 1.50%.

Phosphorus was determined spectrophotometrically as orthophosphate by using a slight modification of the method of Brabson et al.[14] The uncertainty is 0.5% on the amount of phosphorus analyzed.

The glass electrode and saturated calomel electrode pair used in the pH measurement was calibrated with certified NBS buffer standards.[15] The uncertainty in the pH measurements is estimated as 0.015 pH unit.

Calculations. The ion activity product of MHPT defined by

$$I_p = a_{Mg^{2+}} a_{HPO_4^{2-}} \qquad (1)$$

was calculated from the molar activities a_X of the species X in solution

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Table I. Composition and Calculated Quantities[a] of Solutions Equilibrated at 25 °C with $MgHPO_4 \cdot 3H_2O$ in the System $Mg(OH)_2$-H_3PO_4-H_2O

equilibration no.	$10^3 c°_P$, M	$10^3 c_{Mg}$, M	$10^3 c_P$, M	pH	D_R	$10^2 I$, M	$10^3 dE_\pm$, M	$10^6 I_p$, mol²/L²
1	21.9_0	23.5_5	45.3	5.02_2	1.00	7.06	1.24	2.31
2	21.9_0	23.7_5	45.6	5.04_2	1.00	7.12	1.34	2.44
3	16.4_3	18.2_3	34.7	5.22_4	0.99_6	5.48	1.10	2.37
4	16.4_3	18.1_8	34.7	5.23_0	0.99_5	5.47	1.02	2.40
5	10.9_5	12.8_9	23.8	5.50_3	1.00	3.89	1.20	2.42
6	10.9_5	12.9_1	23.9	5.50_6	0.99_7	3.90	1.13	2.45
7	8.21	10.1_5	18.5	5.70_0	0.99_2	3.09	0.94	2.47
8	8.21	10.1_5	18.5	5.69_2	0.99_1	3.09	0.95	2.43
9	5.48	7.49	13.0_9	5.95_9	0.98_3	2.31	0.81	2.48
10	5.48	7.39	12.9_9	5.95_0	0.98_4	2.29	0.75	2.39
11	4.11	6.17	10.3_8	6.13_7	0.98_3	1.93	0.76	2.48
12	4.11	6.14	10.3_3	6.13_2	0.98_6	1.92	0.77	2.43
13	2.74	4.97	7.74	6.40_2	0.99_4	1.60	0.73	2.64
14	2.74	5.00	7.78	6.40_2	0.99_2	1.61	0.75	2.67
15	1.09_5	3.80	4.84	6.90_8	1.01	1.31	0.72	3.05
16	1.09_5	3.79	4.87	6.91_6	1.01	1.31	0.65	3.09
17	0.54_8	3.38	3.91	7.24_3	1.00	1.23	0.46	3.25
18	0.54_8	3.41	3.95	7.24_3	1.00	1.24	0.46	3.30
19	0.109_5	3.30	3.79	7.28_9	0.89_7	1.21	0.41	3.22
20	0.109_5	3.32	3.83	7.27_4	0.89_2	1.21	0.41	3.22

[a] Dissolution ratio D_R (eq 12), ionic strength I (eq 7), deviation from electroneutrality $dE_\pm$ (eq 9), and ion activity product of $MgHPO_4 \cdot 3H_2O$ I_p (eq 1) were calculated by disregarding ion pairs.

by the procedure described by Gregory et al.[16] The thermodynamic dissociation constants at 25 °C for phosphoric acid and for water were taken from Smith and Martell.[17c] The association constants corresponding to the formation of ion pairs, i.e.

$$Mg^{2+} + HPO_4^{2-} \rightleftharpoons MgHPO_4 \qquad (2)$$

$$Mg^{2+} + H_2PO_4^{-} \rightleftharpoons MgH_2PO_4^{+} \qquad (3)$$

are respectively given by

$$K_1 = \frac{a_{MgHPO_4}}{a_{Mg^{2+}} a_{HPO_4^{2-}}} \qquad (4)$$

and

$$K_2 = \frac{a_{MgH_2PO_4^+}}{a_{Mg^{2+}} a_{H_2PO_4^-}} \qquad (5)$$

The activity coefficient y_X of a z_X-valent ion X was estimated by using the Davies approximation[18a]

$$-\log y_X = A z_X^2 \left(\frac{I^{1/2}}{1 + I^{1/2}} - 0.3I \right) \qquad (6)$$

with A a temperature-dependent constant[18b] and I the ionic strength defined by

$$I = \tfrac{1}{2} \sum z_X^2 [X] \qquad (7)$$

where the summation includes all ionic species present in solution and the square brackets denote the molar concentration of the X ion. Because the results of the calculation also reflect the particular approximation chosen for the activity coefficients, calculations were also performed by using the Debye–Hückel equation[18b]

$$-\log y_X = \frac{A z_X^2 I^{1/2}}{1 + B å_X I^{1/2}} \qquad (8)$$

where B is a temperature-dependent constant[18b] and $å_x$ denotes the distance of closest approach for the X ion.[19] Equations 6 and 8 are only valid for dilute electrolyte solutions with an ionic strength up to $I \simeq 0.1$ M,[18] as in the present study.

The best estimates for the thermodynamic solubility product of MHPT, K_{sp}, and for the thermodynamic association constants K_1 and K_2 were calculated by a generalized least-squares procedure simultaneously adjusting the observed values of the observations.[16,20] This procedure, described in greater detail by Gregory et al.,[16] consists of minimizing the weighted sum of squares of residuals of four observations per equilibration (i.e., total molar concentration of magnesium, c_{Mg}, total molar concentration of phosphorus, c_P, initial molar phosphoric acid concentration, $c°_P$, and pH) subject to three condition functions given by

$$dE = \sum z_X [X] \equiv 0 \qquad (9)$$

$$I_p - K_{sp} \equiv 0 \qquad (10)$$

$$D_R - 1 \equiv 0 \qquad (11)$$

with

$$D_R = c_{Mg} / (c_P - c°_P) \qquad (12)$$

the dissolution ratio. In eq 9, defining the deviation from electroneutrality, $dE_\pm$, the summation includes all ionic species present in the system $Mg(OH)_2$–H_3PO_4–H_2O. Equations 9–11, respectively, require for each equilibration that the conditions of electroneutrality, saturation with respect to MHPT, and congruent dissolution of MHPT are satisfied simultaneously. The observations were weighted according to Gregory et al.[16]

Results

Table I summarizes the pH and the analytical concentration of magnesium and phosphorus of the solutions after equilibrating 4–20 g/L of MHPT in dilute phosphoric acid solutions with concentration $c°_P$. The last four columns give D_R and the quantities I, $dE_\pm$, and I_p calculated by using the Davies approximation for the activity coefficients (eq 6) and disregarding ion-pair formation. It is seen from the table that the solution composition of duplicate measurements agrees within experimental error. Moreover, plots of c_{Mg}, c_P, and pH vs. each other, as shown in Figure 1, yield smooth curves, indicating

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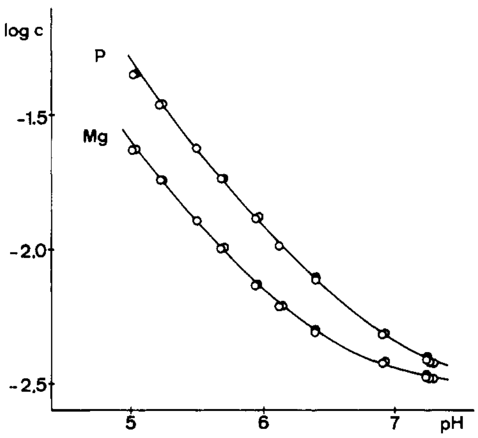

Figure 1. Logarithm of the analytical concentrations of magnesium (Mg) and phosphorus (P) plotted against pH. The curves represent the solubility isotherms at 25 °C calculated according to the generalized least-squares method.

the internal consistency of the results.

With the exception of equilibrations 19 and 20, the dissolution ratio D_R equals, within experimental error, the stoichiometric 1:1 ratio required for a congruent dissolution. Moreover, for these equilibrations the X-ray diffraction pattern of the solid remained qualitatively and quantitatively unchanged after equilibration, indicating that no recrystallization occurred. For equilibrations 19 and 20 the patterns of the solid after equilibration showed some weak additional reflections corresponding to the most intense reflections of bobierrite, $Mg_3(PO_4)_2{\cdot}8H_2O$.[21] Apparently, in experiments 19 and 20 bobierrite was formed during the equilibration of MHPT according to

$$2[MgHPO_4{\cdot}3H_2O(s)] + Mg^{2+}(aq) + 2H_2O \rightarrow Mg_3(PO_4)_2{\cdot}8H_2O(s) + 2H^+(aq) \quad (13)$$

resulting in a lower D_R value and an apparent decrease in solubility.

Table I shows that for all equilibrations $dE_\pm$ is positive and significantly greater than the anticipated experimental error. Moreover, $dE_\pm$ depends on the solution composition, decreasing with increasing pH. Within experimental error the ion activity product of MHPT is independent of the solution composition up to pH ~6; above this pH, I_p significantly increases with increasing pH. The same dependency of $dE_\pm$ and I_p on the solution composition is found when the activity coefficients are estimated with the Debye–Hückel equation (eq 8). These observations indicate that the formation of ion pairs cannot be neglected in the calculations.

From the analytical data in Table I, the best estimates of the thermodynamic solubility product K_{sp} and the association constants K_1 and K_2 were obtained by the generalized least-squares procedure. Since the condition given by eq 11 is not satisfied for equilibrations 19 and 20, the corresponding analytical data were not included in the calculations. The activity coefficients were approximated with the Davies equation (eq 6) or with the Debye–Hückel equation (eq 8). In both cases the calculation converges, resulting in the estimates of K_{sp}, K_1, and K_2 with a standard deviation of the adjustment, s, as given in Table II. For 51 degrees of freedom, the values of 42.2 and 43.0 found for χ^2 when the Davies and Debye-Hückel approximations, respectively, are used, lie well within the critical range of $\chi^2_{95\%}$, 33.17–72.61, indicating the goodness of fit.[20] Table II shows that the estimates of K_{sp}, K_1, and K_2 statistically do not significantly differ when the activity coefficients are calculated with the Davies equation or with the Debye–Hückel equation.

Table II. Solubility Product and Association Constants Calculated according to the Generalized Least-Squares Method Using the Davies and Debye–Hückel Equations for Activity Coefficients

	$10^6 K_{sp}$, mol^2/L^2	K_2, M^{-1}	K_1, M^{-1}	$10^5 s$,[b] M
Davies	$1.67_2 \pm 0.03_2$[a]	18.9 ± 1.7	712 ± 23	9.1 ± 0.9
Debye–Hückel	$1.70_2 \pm 0.03_3$	24.0 ± 1.7	707 ± 23	9.2 ± 0.9

[a] Standard deviation according to the generalized least-squares method. [b] Standard deviation of the adjustment with dispersion as defined in ref 16.

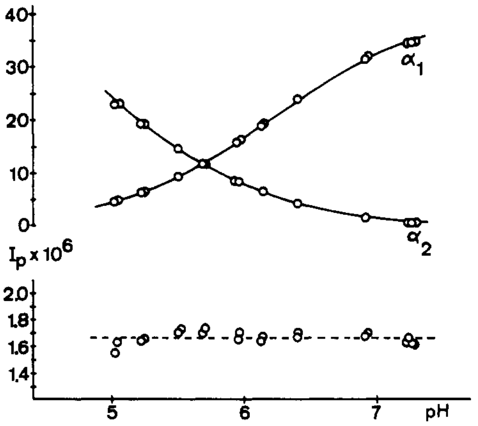

Figure 2. Above: Fraction of magnesium present as ion pairs according to eq 14 and 15. Below: Ion activity product of $MgHPO_4{\cdot}3H_2O$ corrected for ion-pair formation plotted against pH.

With only a few exceptions, the adjustments on the observations are smaller than the anticipated experimental error on the analytical figures. Only the adjustment of the pH of equilibration 1 differs statistically significantly from the anticipated experimental error. Disregarding the data of equilibration 1 in the calculation results in estimates of K_{sp}, K_1, and K_2 that agree within the reported error with the data presented in Table II. The agreement between calculated and measured data is seen in Figure 1, where the solid lines correspond to the values of c_{Mg}, c_P, and pH adjusted on the basis of the Davies equation and the conditions given by eq 9–11.

By use of the values for K_1 and K_2 given in Table II and the Davies approximation for the activity coefficients, I_p and the fraction of Mg present as ion pairs were calculated from the analytical data in Table I. The results are represented in Figure 2 where

$$\alpha_1 = 100[MgHPO_4]/c_{Mg} \quad (14)$$

and

$$\alpha_2 = 100[MgH_2PO_4^+]/c_{Mg} \quad (15)$$

denote the fraction of Mg present as $MgHPO_4$ and $MgH_2PO_4^+$ ion pairs respectively. The broken line corresponds to the value of K_{sp} given in Table II. A calculation based on the Debye–Hückel equation results in the same picture as shown in Figure 2. From the figure it is seen that the dependency of I_p on the solution composition, as noted from Table I, disappears when the formation of $MgHPO_4$ and $MgH_2PO_4^+$ ion pairs is taken into account. Moreover, the figure clearly shows that the concentration of $MgH_2PO_4^+$ cannot be neglected at low pH values.

Discussion

The consistency of the data, the smoothness of the solubility isotherms, and the convergency of the generalized least-squares procedure in the calculation of K_{sp} over a wide range of solution compositions indicate that the MHPT sample dissolves congruently and is in equilibrium with the aqueous phase after

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(21) ASTM Powder Diffraction Data File No. 16-330.

the equilibration. Consequently, the present data are representative for the solubility behavior of a stoichiometric and well-crystalline $MgHPO_4·3H_2O$ sample free from extraneous phases.

The dependence of the ion activity product of MHPT on the solution composition as seen from Table I is consistent with the formation of the ion pairs $MgH_2PO_4^+$ and $MgHPO_4$. In fact, the fraction of magnesium present as ion pairs, i.e. the sum of α_1 and α_2 (eq 14 and 15 and Figure 2), shows the same trend with respect to pH as the ion activity products given in Table I. Figure 2 shows that when ion-pair formation is taken into account, the ion activity product becomes independent of pH and equals the thermodynamic solubility product.

As mentioned in the Introduction, several investigators have studied the ion-pair formation between magnesium and orthophosphate species. In general, the experimental data could be accounted for on the assumption that $MgH_2PO_4^+$ and/or $MgHPO_4$ are present in acidic to neutral aqueous solutions.[5,7,8,10,11] More direct evidence for the formation of these ion pairs is given by the conductance data of Tabor and Hastings[22] and the electromigration experiments of Kulba et al.[9]

Childs[10] titrated aqueous solutions containing H_3PO_4 and $Mg(NO_3)_2$ with KOH at 37 °C using 0.15 M KNO_3 to keep the ionic strength constant. A least-squares analysis showed that the best fit of his pH measurements was obtained when the species $MgH_3(PO_4)_2^-$ and $MgH_2(PO_4)_2$ also were included in the solution model. In view of the rather high concentrations of phosphate and Mg^{2+} (9×10^{-4} up to 8.4×10^{-3} M) as compared to that of the supporting electrolyte KNO_3, the improvement in fit by accepting the presence of such polynuclear species can also be due to compensating errors, the latter arising from a change in activity coefficients. Havel and Högfeldt[11] performed quite similar titrations in the medium $[NaClO_4 + Mg(ClO_4)_2] = 3$ M. These authors only found some indication of the formation of the dimer $MgH_2(PO_4)_2$ but considered it too uncertain for the existence of this species to be regarded as confirmed. According to Havel and Högfeldt the improvement in fit could equally well be obtained by taking into account the change in activity coefficients on replacement of Na^+ with Mg^{2+} in such media of high ionic strength. In the present study it was not necessary to introduce such additional ion pairs in order to obtain statistically acceptable values for K_{sp}, K_1, and K_2.

A comparison of the association constants listed in Table II with literature values is rather difficult. In general, apparent association constants were determined by using experimental conditions that varied from investigation to investigation.[9-12,17,23-27] Since the value of an apparent association constant depends not only on the quantitative but also on the qualitative composition of the medium, a direct comparison with the association constants K_1 and K_2 found in the present study is not feasible. However, Turner et al.[28] compiled and evaluated a critical data base from literature data. According to this data base the apparent association constants of $MgH_2PO_4^+$ and $MgHPO_4$ at infinite dilution and 25 °C are 14.8 and 759 M^{-1}, respectively, which agree with the values given in Table II.

The value for K_1 in Table II lies between the values 512 and 806, respectively, reported by Clarke et al.[7] and Taylor et al.[5] The former performed potentiometric measurements in a rather restricted pH range, i.e. $6.2 < pH < 6.7$, using the molal concentration scale, whereas the latter obtained K_1 from a solubility study of MHPT. In both studies the concentration of $MgH_2PO_4^+$ was assumed to be negligible. According to Figure 2, this assumption certainly does not hold in the pH range $5.2 < pH < 7.4$ used by Taylor et al.[5] Consequently, their estimate of K_1 will be somewhat too high.

A comparison of the association constants of $MgH_2PO_4^+$ and $MgHPO_4$ in Table II with those of the corresponding calcium–phosphate ion pairs[16,29-31] shows that the latter are smaller. This agrees with the general trend found in the literature.[6,10,12,24,28,32] Moreover, it is consistent with the expectation for ion-pair formation in which purely electrostatic bonding predominates; i.e., the association constant will decrease with increasing cation size.

Some investigators have determined an apparent solubility product for MHPT.[8,22,33] However, as Holt et al.[34] properly pointed out, the results of Greenwald[33] and Tabor and Hastings[22] cannot be regarded as representative for the solubility behavior of pure and well-crystalline $MgHPO_4·3H_2O$. In both studies no characterization of the solid is given nor is the stoichiometry of the dissolution reaction controlled. In view of the relatively high pH values reported in these solubility studies, the possibility cannot be ruled out that a more basic magnesium phosphate is the solubility-controlling phase (see, e.g., equilibrations 19 and 20 in Table I).

Racz et al.[4,35] determined the solubility of a MHPT sample by equilibrating the solid in water, $MgCl_2$ solutions, and HCl solutions at 25 °C. Taking into account the formation of $MgHPO_4$ ion pairs, a constant value of 1.48×10^{-6} mol^2/L^2 was found for the thermodynamic solubility product of $MgHPO_4·3H_2O$ over a rather restricted pH range. This value is slightly lower than that found in the present study. However, the composition of the sample used by Racz et al.[35] deviates significantly from that required by the $MgHPO_4·3H_2O$ stoichiometry. Moreover, when the dissolution ratio is calculated from their data, D_R values are found which are mostly lower than unity and which decrease with increasing concentration of the $MgCl_2$ used for the equilibration. Considering the solution compositions and the hydrolysis experiments of MHPT performed by Duff,[36] this is a strong indication that during the equilibrations of Racz et al.[4] $Mg_3(PO_4)_2·8H_2O$ is formed according to eq 13. Consequently, the final solution compositions found by Racz et al. may have been controlled by this phosphate.

Although Taylor et al.[5] neglect the formation of $MgH_2PO_4^+$ ion pairs, their value of $(1.5 \pm 0.1) \times 10^{-6}$ mol^2/L^2 for the thermodynamic solubility product of MHPT is in good agreement with the estimate found in the present study. A recalculation of the ion activity product of MHPT from their data, taking into account the association constants given in Table II and using the Davies approximation for the activity coefficients, results in I_p values of 1.3×10^{-6} and 1.5×10^{-6} mol^2/L^2 at pH ~5.30 and 6.8, respectively. Apparently, I_p depends slightly on the solution composition and is somewhat smaller than the K_{sp} value 1.67×10^{-6} of Table II. Since Taylor et al.[5] also equilibrated their sample until a constant I_p was obtained, these differences most probably are due to the single-point calibration of the glass–reference electrode

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pair with a potassium biphthalate buffer of pH 4.00 in their pH measurements as compared to the multipoint standardization used in the present study. It is known that in practical pH measurements the potential–pH slope of glass–reference electrode pairs mostly is less than the theoretical slope.[37,38] Consequently, the pH measured on the basis of a single-point calibration will systematically differ from the actual pH, the deviation being greater, the greater the difference between the actual pH and the calibration pH.[38,39] On this basis and in view of the rather severe restrictions imposed on the analytical data by the least-squares adjustment, the estimates of the thermodynamic solubility product of $MgHPO_4 \cdot 3H_2O$ and of the association constants of $MgH_2PO_4^+$ and $MgHPO_4$ obtained in the present study form a consistent and more reliable set of constants.

Registry No. $MgHPO_4 \cdot 3H_2O$, 7782-75-4.

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Electrochemical Study of Tungsten Chloro Complex Chemistry in the Basic Aluminum Chloride–1-Methyl-3-ethylimidazolium Chloride Ionic Liquid

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Absorption spectroscopy indicated that the addition of WCl_6 or $KWCl_6$ to the basic aluminum chloride–1-methyl-3-ethylimidazolium chloride ionic liquid produced the tungsten(V) chloro complex $[WCl_6]^-$. This species can be reduced to $[WCl_6]^{2-}$ and $[WCl_6]^{3-}$ via two consecutive, reversible, one-electron reduction processes with voltammetric half-wave potentials of 0.45 and −0.80 V, respectively, referenced to aluminum in 66.7:33.3 mol % melt. The metal-bonded tungsten(III) dimer $[W_2Cl_9]^{3-}$ exhibited two one-electron voltammetric oxidation waves with half-wave potentials of −0.07 and 0.43 V, respectively. The first wave corresponded to the formation of $[W_2Cl_9]^{2-}$ and was reversible and uncomplicated on the voltammetric time interval. The second wave did not exhibit a reverse current. However, the oxidation of $[W_2Cl_9]^{3-}$ consumed two electrons per mole of $[W_2Cl_9]^{3-}$ on the time interval encompassed by controlled-potential coulometry and $[WCl_6]^{2-}$ was the sole product. This suggested that coulometric oxidation of $[W_2Cl_9]^{3-}$ follows an ECE pathway with the following steps: (1) one-electron oxidation of $[W_2Cl_9]^{3-}$ to $[W_2Cl_9]^{2-}$, (2) slow disproportionation of $[W_2Cl_9]^{2-}$ to $[WCl_6]^{2-}$ and a tungsten(III) complex, and (3) one-electron oxidation of the tungsten(III) complex to $[WCl_6]^{2-}$. The Stokes–Einstein equation was applicable to $[WCl_6]^-$, $[WCl_6]^{2-}$, and $[W_2Cl_9]^{3-}$ over a large range of melt composition. Diffusion coefficients for these species in 44.4 mol % melt at 40.0 °C were $(2.8 \pm 0.2) \times 10^{-7}$, $(2.2 \pm 0.1) \times 10^{-7}$, and $(1.5 \pm 0.1) \times 10^{-7}$ $cm^2\ s^{-1}$, respectively. Close agreeement was obtained between experimental solvodynamic and calculated structural radii for both $[WCl_6]^-$ and $[WCl_6]^{2-}$, which suggested that these species were essentially unsolvated in the melt.

Introduction

Aluminum chloride can be combined with certain organic salts to produce ionic liquids at room temperature. Familiar examples of such liquids are mixtures of aluminum chloride with 1-*n*-butylpyridinium chloride (BPC) or 1-methyl-3-ethylimidazolium chloride (MEIC).[1,2] Both systems have been found to be good solvents for electrochemistry and spectroscopy. The Lewis acid–base properties of these ionic liquids can be varied by adjusting the ratio of $AlCl_3$ to organic salt. Melts in which the apparent mole fraction of $AlCl_3$ exceeds 0.5 are acidic, owing to the presence of the heptachloroaluminate ion, which is a chloride ion acceptor. Those melts with an $AlCl_3$ mole fraction less than 0.5 are basic, since they contain uncomplexed chloride ion.

The results obtained during previous studies indicate that transition-metal ions form very stable anionic chloro complexes in basic $AlCl_3$–BPC or basic $AlCl_3$–MEIC.[3-11] Tetrahedral $[MCl_4]^{n-4}$ chloro complex anions were found for most dipositive and tripositive 3d ions in these melts.[3-8] A series of $[MCl_p]^{1-p}$ complexes with $2 \leq p \leq 4$ were detected for copper(I)[8] and silver(I).[9] Titanium(IV), octahedrally complexed as $[TiCl_6]^{2-}$, was found to exist in equilibrium with an oxychloro complex, $[TiOCl_4]^{2-}$, when oxide ion was introduced into the melt by dissolution of Li_2CO_3.[10] Basic $AlCl_3$–MEIC was found to be a useful solvent for stabilizing the $[MoCl_6]^{2-}$ ion, which had not been studied in solution previously.[11]

Several studies have been concerned with the chemistry of tungsten chloro complex solutes in alkali-metal chloride based chloroaluminate melts,[12-14] molten alkali-metal chlorides,[15-17] and conventional aprotic solvents.[18,19] Marshall and Yntema[12] examined the deposition of tungsten metal from fused Al-

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