# Comparative Study of Sodium Phosphate and Sodium Sulfate in Aqueous Solutions at (298.15 to 353.15) K

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ABSTRACT: The binary and ternary aqueous solutions of sodium phosphate or/and sulfate were studied using the hygrometric method from dilution to saturation in the temperature range from (298.15 to 353.15) K. The hygrometric measurements of the binary systems were combined with reference pure water, $Na_3PO_4(s)$, and $Na_2SO_4(s)$ solubility data to construct a chemical model that calculates solute and solvent activities from dilute to saturated solution concentration (for ($Na_3PO_4(s)$) up to m_{max} = 9.00 mol·kg^{-1} at 353.15 K; and up to $m_{max}(Na_2SO_4(s))$ = 3.40 mol·kg^{-1}at 313.15 K). The constructed model was also used to calculate thermodynamic solubility product (K°_{sp}) of $Na_3PO_4(s)$ and $Na_2SO_4(s)$ in the temperature range (298.15 to 353.15) K. The excess Gibbs energies of $Na_3PO_4(aq)$ and $Na_2SO_4(aq)$ were evaluated at various temperatures. The results for these aqueous solutions were influenced by the effect of hydration shell, with ion association or formation ion pairing. The anion solute PO_4 or SO_4 influences the hydration in an aqueous solution; indeed the hydrogen bonding of water in the hydration shells of PO_4^{3-} anion is preeminent over that of SO_4^{2-}. The mixed electrolyte solutions $\{(yNa_3PO_4 + (1 - y)Na_2SO_4)(aq)\}$ were also investigated in the temperature range from (298.15 to 353.15) K and at total molalities from dilution (0.10 mol·kg^{-1}) to saturation for different ionic-strength fractions (y) of Na_3PO_4 with y = 0.20, 0.50, and 0.80. The water activity of mixed salts solutions and related properties such as osmotic and activity coefficients were carried out at various temperatures. The osmotic coefficients data were used to evaluate the mixing parameters of the ion interaction model θ_{MN} and ψ_{MNX} in the ternary system $Na_3PO_4 + Na_2SO_4 + H_2O$.
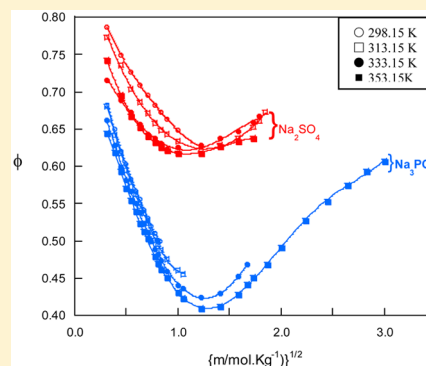
1. INTRODUCTION

The optimization of operating conditions and investment in industries of wet process phosphoric acid (WPPA) require a comprehensive and accurate determination of the phase behavior of these minerals to attempt a better comprehension of the mechanisms and physicochemical conditions of their formation: temperature, pressure, concentration.[1−3] Mastering and controlling the formation of these minerals will contribute to the improvement of the phosphoric acid production process during the reaction step, filtrations, and concentration. Some notable areas of interest are the thermo-chemical data for hydrolyzed ions in aqueous solutions,[4] the methods of extrapolation above standard temperature and pressure, and the treatment of equilibria complex solids. Therefore, phosphate and sulfate salts are important components found in the process and recovery of phosphates, during the attack of phosphate rock with sulfuric acid to produce phosphoric acid. The knowledge of the thermodynamic properties of aqueous solutions of phosphate and/or sulfate salts is essential to understand the interaction of aqueous solutions with minerals encountered in phosphate industry.[5−7] Various chemical and biochemical processes request the knowledge of the properties of aqueous solutions including those of the SO_4 and PO_4 anions.[8−11]

The ambient temperature (298.15 K) thermodynamic activity data for $Na_2SO_4(aq)$ are largely given by many authors and several methods have been used such as isopiestic, calorimetric, emf, dsvp, dvp.[12−26]

Rard et al.[16] presented for $Na_2SO_4(aq)$ a critical analysis of the available thermodynamic data obtained by various techniques. They recalculate them in a consistent manner and use the more reliable results to evaluate the parameters of both an Archer-type modified Pitzer model and a similar model using mole fraction compositions. The hygrometric measurements of the aqueous solutions of $Na_2SO_4 \cdot 10H_2O$ were also performed at 298.15 K[27] and compared with the literature data.[13,16,28,29] The summary of available literature data for $Na_2SO_4(aq)$ in a molality range at various temperatures, was presented in Table 1.[16,30−39] Indeed, Holmes and Mesmer reported high-temperature isopiestic data from (383.15 to 498.15) K[30] and up to 498.15 K.[31] Isopiestic vapor-pressure measurements were also made by Rard et al.[16] at 323.15 K and by Baabor et al.[32,33] at 313.15 K. The emf studies were given at temperatures from (273.15 to 313.15) K in the molality range (0.075 to 1.3) mol·kg^{-1},[38] and for (0.001 to 0.30) mol·kg^{-1} from (283.15 to 343.15) K.[39]

In our recent article of thermodynamic properties of binary aqueous solutions of orthophosphate salts, sodium, potassium, and ammonium at T = 298.15 K,[40] measurements of aqueous solutions of $Na_3PO_4-H_2O$ were performed at T = 298.15 K from dilution (0.10 mol·kg^{-1}) to saturation solution. The comparison

 A

Table 1. Summary of Literature Data for Na$_2$SO$_4$(aq) at Various Temperatures

range of molality mol·kg^{-1}	T/K	method	ref
0.12 to 3.6	323.15	isopiestic	16
0.5 to 3.5	383.15 to 498.15	isopiestic	30
0.1 to 3.0	273.15 to 498.15		31
0.14 to 3.3	313.15	isopiestic	32, 33
0.21 to 3.3			
0.91 to 3.4	333.15	isopiestic	34
0.70 to 2.97	353.15	isopiestic	35
0.47 to 1.85	323.15 to 423.15	SVP	36
0.29 to 3.2	423.15 to 523.15		37
0.075 to 1.3	273.15 to 313.15	emf	38
0.001 to 0.30	283.15 to 343.15	emf	39

between these results and those of the literature was given,[41] and good agreement was obtained. However, no available data exists for this system at high temperature.

This paper continues our series[42,43] concerning experimental determination of water activity and osmotic coefficients in binary and mixed aqueous solutions from low to high concentration using the hygrometric method, and parametrization of XT-variable thermodynamic models for experimentally studied systems. The main objectives are the determination of water activity and osmotic coefficients of the binary and ternary solutions, respectively, Na$_3$PO$_4$–H$_2$O, Na$_2$SO$_4$–H$_2$O, and Na$_3$PO$_4$ + Na$_2$SO$_4$ + H$_2$O from dilution to saturation, and from T = (298.15 to 353.15) K on the basis of hygrometric measurements. The behavior and comparison of anion effects of PO$_4^{3-}$ and SO$_4^{2-}$ in aqueous solutions were also examined. The thermodynamic properties were investigated for the binary systems in the temperature range from T = (298.15 to 353.15) K and from dilute up to saturated solution. The mixed salts solutions {yNa$_3$PO$_4$ + (1−y)Na$_2$SO$_4$}(aq) were also investigated using the hydrometric method in the temperature range (298.15 to 353.15) K and at total molalities from dilution to saturation for different ionic-strength fractions (y) of Na$_3$PO$_4$ with y = 0.20, 0.50, and 0.80.

2. EXPERIMENTAL SECTION

2.1. Apparatus. The experimental water activity was determined using the hygrometric method previously described in earlier works.[42,43] The apparatus used is based on the measurement of the water activity over an aqueous solution containing nonvolatile electrolytes. For the water activity measurements of the aqueous electrolytes at different temperatures ranging from (298.15 to 353.15) K, the apparatus was modified and adapted to elevated temperatures.[44] The droplets of a reference solution of NaCl(aq) or LiCl(aq) are deposited on the spider thin thread by atomization. This thread is kept tense over a perspex support, which was fixed to a cup containing the selected studied solution. The cup was then placed in a thermostated box. The apparatus was held at a constant temperature, the standard uncertainty of temperature was $u(T)$ = 0.1 K. The droplet diameter was measured by a microscope with an ocular equipped with a micrometric screw. Several measurements were performed of the spherical drops diameters and the mean results which are repeats. For each molality five and more cups were taken, and for each cup 5 to 6 measurements were made adequately to determine the average diameter. The relative standard uncertainty in the water activity depends on the accuracy of the diameter measurements and is therefore $u_r(a_w)$ = 0.0002 for a_w > 0.97; $u_r(a_w)$ = 0.0005 for

0.97 > a_w > 0.95; $u_r(a_w)$ = 0.0009 for 0.95 > a_w > 0.90, and $u_r(a_w)$ = 0.002 for a_w < 0.90.

2.2. Material and Solution. The solutions of Na$_3$PO$_4$(aq) and Na$_2$SO$_4$(aq) and their mixtures were prepared from anhydrous materials by Riedel-de-Haën(RH), Sigma-Aldrich (SA), with mass % of purity of Na$_3$PO$_4$·12H$_2$O (≥98%, SA) and Na$_2$SO$_4$ (99%, RH), and double-distilled water (conductivity <5 μS·m^{-1}). The molality is prepared at the considered value in the binary and ternary systems and its standard uncertainty is $u(m)$ = 0.01 mol·kg^{-1}.

3. RESULTS

3.1. Binary Systems. *3.1.1. Water Activity and the Osmotic Coefficient of the Water.* The measurement of the water activities of the binary systems Na$_3$PO$_4$−H$_2$O and Na$_2$SO$_4$−H$_2$O were performed using the hygrometric method from dilution up to saturation solutions in the temperature range from T = (298.15 to 353.15) K. The experimental results of the water activity were used to determine the osmotic coefficients of the water by

$$\phi = -\left(\frac{1000}{M_w \cdot \sum_i \nu_i m_i}\right) \ln a_w \tag{1}$$

where ν_i is the number of ions released by dissociation, m_i is the molality of solute i; and M_w is the molar mass of water.

The experimental water activities of the Na$_3$PO$_4$(aq) and Na$_2$SO$_4$(aq) were given in Table 2. The values of water activity are very similar in the temperature range from (298.15 to 353.15) K until a molality of 0.40 mol·kg^{-1} for Na$_3$PO$_4$(aq) and 0.20 mol·kg^{-1} for Na$_2$SO$_4$(aq). Indeed, the water activities of these solutions decrease at elevated temperatures. In addition, the calculated osmotic coefficients are presented in Table 2 and shown as a function of square root of ionic strength $I^{1/2}$ at various temperatures (Figure 1). These coefficients decrease with molality until (2.00 to 2.20) mol·kg^{-1} for Na$_2$SO$_4$(aq) and increase in concentrated solution. However, they decrease for Na$_3$PO$_4$(aq) and increase until the molality 2.50 mol·kg^{-1} at (333.15 to 353.15) K.

Discussion. The comparison of Na$_3$PO$_4$(aq) and Na$_2$SO$_4$(aq) behaviors in aqueous solutions was made over the ranges of molality and temperature from (298.15 to 353.15) K. Figure 2 shows that the osmotic coefficients of Na$_2$SO$_4$(aq) are higher than those of Na$_3$PO$_4$(aq), and they decrease at a dilute-moderate concentration and increase in concentrated solutions. The anion effect is considered at various temperatures from (298.15 to 353.15) K, and these coefficients are as follow:

$$\phi_{Na_2SO_4(aq)} > \phi_{Na_3PO_4(aq)}$$

Indeed, the quantity of water molecules required to hydrate the solute ions increases with the decrease of free molecules of solvent. Therefore, the amount of solvent which overcomes the vapor phase diminishes, and the salt having the lowest water activity is the most extensively hydrated in the solution. In the light of their reduced water activities, multiply charged cations seem to be more extensively hydrated than the singly charged cations.[27,40]

This magnitude indicates that sodium phosphate (1−3 charge -type) solutions are more hydrated than those of sulfate (1−2 charge-type). Some hypotheses could be also suggested for the structure of these salts in aqueous solutions over the range of molality and at various temperatures. Indeed, the literature

Table 2. Water Activities, Osmotic and Activity Coefficients of the Binary Aqueous Solutions of Na$_3$PO$_4$–H$_2$O and Na$_2$SO$_4$–H$_2$O as Function of Molality m at Different Temperatures from (298.15 to 353.15) K and Pressure (P = 0.1 MPa^a)

$T/K =$	298.15			313.15			333.15			353.15		
m/ mol· kg^{-1}(H$_2$O)	a_w	ϕ	γ	a_w	ϕ	γ	a_w	ϕ	γ	a_w	ϕ	γ
					Na$_2$SO$_4$–H$_2$O							
0.10	0.9958	0.787	0.450	0.9958	0.773	0.412	0.9961	0.715	0.382	0.9960	0.742	0.372
0.20	0.9919	0.749	0.369	0.9920	0.736	0.328	0.9925	0.688	0.295	0.9925	0.696	0.288
0.30	0.9883	0.726	0.324	0.9886	0.704	0.282	0.9891	0.673	0.250	0.9892	0.667	0.243
0.40	0.9848	0.709	0.293	0.9852	0.686	0.253	0.9859	0.656	0.220	0.9859	0.653	0.215
0.50	0.9814	0.695	0.270	0.9820	0.671	0.231	0.9827	0.643	0.201	0.9828	0.640	0.194
0.60	0.9781	0.682	0.252	0.9788	0.658	0.214	0.9795	0.637	0.186	0.9797	0.632	0.179
0.70	0.9749	0.672	0.238	0.9757	0.649	0.201	0.9764	0.631	0.174	0.9766	0.625	0.166
0.80	0.9717	0.663	0.226	0.9725	0.643	0.189	0.9732	0.623	0.164	0.9734	0.622	0.156
1.00	0.9656	0.648	0.206	0.9663	0.633	0.172	0.9667	0.625	0.150	0.9672	0.617	0.140
1.20	0.9560	0.637	0.191	0.9593	0.628	0.139	0.9601	0.624	0.138	0.9604	0.616	0.128
1.50	0.9504	0.627	0.175	0.9505	0.626	0.144	0.9503	0.628	0.128	0.9511	0.618	0.115
1.80	0.9404	0.622	0.162	0.9408	0.627	0.121	0.9395	0.638	0.122	0.9409	0.623	0.105
1.97	0.9347	0.625	0.158									
2.00				0.9343	0.628	0.127	0.9334	0.637	0.118	0.9344	0.627	0.099
2.20				0.9275	0.631	0.115	0.9263	0.641	0.116	0.9278	0.630	0.095
2.50				0.9175	0.637	0.116	0.9162	0.647	0.113	0.9180	0.633	0.087
2.80				0.9074	0.645	0.111	0.9061	0.654	0.112	0.9080	0.637	0.081
3.00				0.8996	0.652	0.108	0.8986	0.659	0.111	0.9017	0.638	0.078
3.20				0.8919	0.661	0.105	0.8910	0.667	0.115			
3.40				0.8836	0.673	0.103						
					Na$_3$PO$_4$–H$_2$O							
	b	b	b									
0.10	0.9951	0.682	0.256	0.9951	0.681	0.216	0.9952	0.662	0.207	0.9954	0.645	0.205
0.15	0.9930	0.650	0.217	0.9931	0.642	0.179	0.9932	0.628	0.171	0.9933	0.619	0.170
0.20	0.9911	0620	0.193	0.9911	0.618	0.155	0.9914	0.599	0.148	0.9915	0.593	0.148
0.25	0.9892	0.603	0.171	0.9893	0.595	0.138	0.9896	0.581	0.131	0.9898	0.570	0.131
0.30	0.9875	0.582	0.162	0.9876	0.579	0.125	0.9878	0.566	0.119	0.9880	0.555	0.119
0.35	0.9858	0.567	0.144	0.9859	0.563	0.115	0.9862	0.550	0.109	0.9865	0.539	0.109
0.40	0.9841	0.556	0.133	0.9844	0.547	0.106	0.9846	0.538	0.101	0.9850	0.524	0.100
0.45	0.9826	0.541	0.125	0.9827	0.537	0.099	0.9832	0.524	0.093	0.9835	0.513	0.093
0.50	0.9811	0.530	0.117	0.9813	0.524	0.093	0.9817	0.512	0.088	0.9820	0.504	0.087
0.55	0.9794	0.525	0.111	0.9799	0.511	0.087	0.9804	0.500	0.082	0.9807	0.439	0.082
0.60	0.9782	0.501	0.105	0.9785	0.501	0.083	0.9791	0.489	0.078	0.9795	0.479	0.077
0.65	0.9768	0.501	0.100	0.9771	0.495	0.078	0.9777	0.482	0.074	0.9782	0.470	0.073
0.68	0.9758	0.500	0.097	0.9762	0.490	0.075	0.9768	0.477	0.072	0.9777	0.465	0.071
0.70				0.9757	0.487	0.075	0.9764	0.474	0.070	0.9770	0.462	0.070
0.80				0.9730	0.475	0.068	0.9739	0.459	0.064	0.9743	0.451	0.063
1.00				0.9673	0.461	0.058	0.9687	0.441	0.055	0.9694	0.431	0.054
1.10				0.9646	0.455	0.054	0.9660	0.436	0.051	0.9671	0.423	0.045
1.50							0.9552	0.424	0.041	0.9568	0.409	0.040
2.00							0.9399	0.430	0.032	0.9424	0.412	0.032
2.50							0.9218	0.452	0.026	0.9258	0.428	0.027
2.80							0.9098	0.468	0.023	0.9146	0.442	0.025
3.00										0.9071	0.451	0.023
3.50										0.8884	0.469	0.021
4.00										0.8679	0.492	0.018
5.00										0.8271	0.527	0.015
6.00										0.7873	0.553	0.012
7.00										0.7482	0.575	0.010
8.00										0.7104	0.593	0.008
9.00										0.6745	0.607	0.007

^{a}Standard uncertainty of temperature is $u(T)$ = 0.1 K and molality is $u(m)$ = 0.01 mol·kg^{-1}. The relative standard uncertainty is $u_r(a_w)$ = 0.0002 for a_w > 0.97; $u_r(a_w)$ = 0.0005 for 0.97 > a_w > 0.95; $u_r(a_w)$ = 0.0009 for 0.95 > a_w > 0.90 and $u_r(a_w)$ = 0.002 for a_w < 0.90. Standard uncertainty of osmotic coefficient ϕ is estimated at $u(\phi)$ = 0.005. (N = 13 to 19 for Na$_2$SO$_4$; N = 13 to 29 for Na$_3$PO$_4$) number of experimental data points (each point is the average of 8 to 10 series of experiments). For Na$_3$PO$_4$ at 298.15 K. ^{b}Data from ref [40].

indicates an extensive hydration of phosphate and sulfate anions in solution.[45−49] Furthermore, there is no evidence for liaison between phosphate anions and the cation of sodium.[50]

However, the possibility of association and anion pairing should be considered at high concentration. Moreover, from Raman spectroscopy in combination with a resolution of the multivariate

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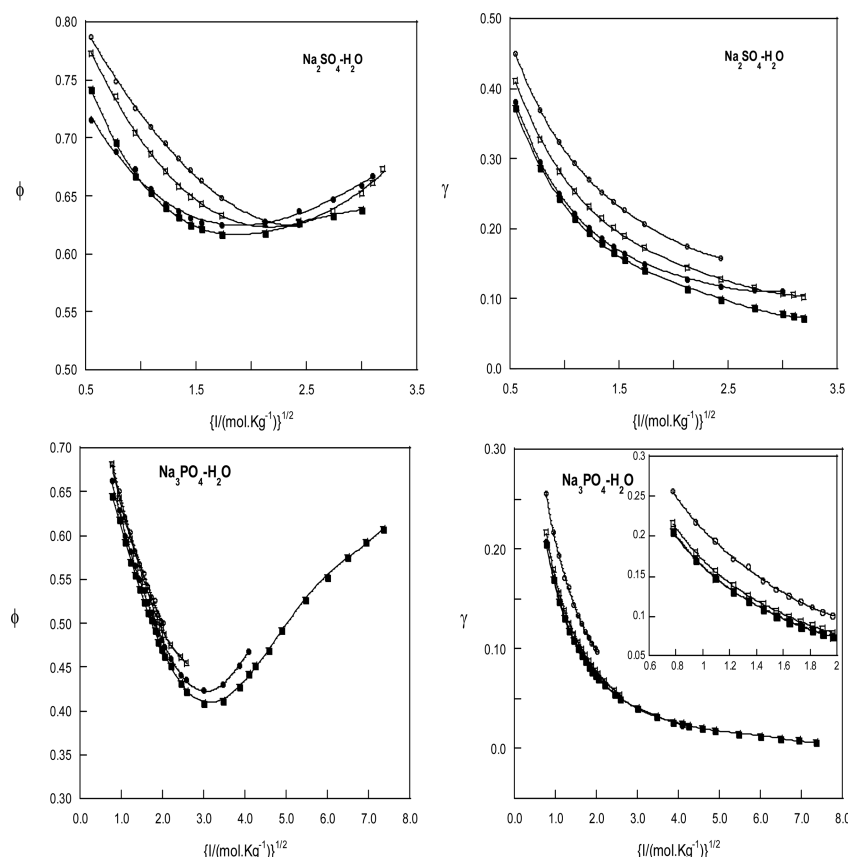
Figure 1. Osmotic and activity coefficients of $Na_2SO_4(aq)$ and $Na_3PO_4(aq)$ as function $I^{1/2}$ at different temperatures: (○) 298.15 K; (□) 313.15 K; (●) 333.15 K; (■) 353.15 K.
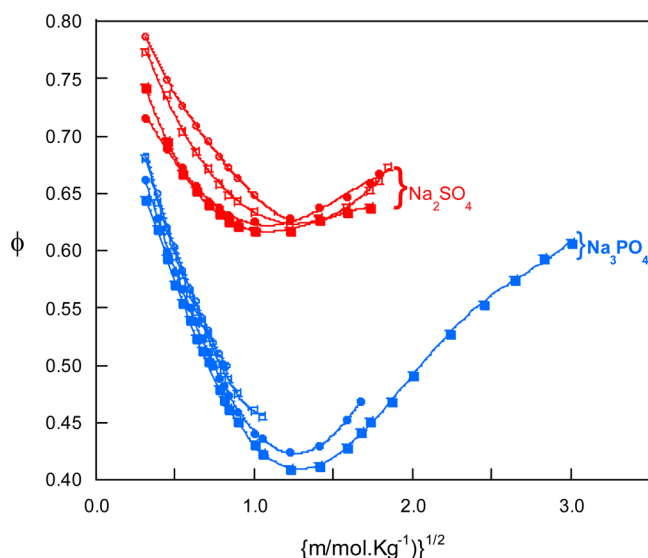
Figure 2. Comparison of osmotic coefficients as a function of $m^{1/2}$ of the binary solutions $Na_2SO_4(aq)$ and $Na_3PO_4(aq)$: in various ranges of molality and temperature (○) 298.15 K; (□) 313.15 K; (●) 333.15 K; (■) 353.15 K.

curve, Ahmed et al.[51] studied how ions affect the structure of water to examine the interaction between water and various kosmotropic and chaotropic anions. The Raman-MCR of aqueous Na-salt (NaI, NaBr, NaNO₃, Na₂SO₄, and Na₃PO₄) solutions stipulates solute-correlated Raman spectra of water. The SC-spectra predominantly wear the vibrational

characteristics of water in the hydration shell of anions, because the Na^+ cation has negligible effect on the OH stretch band of water. The wavenumber of the average peak area of the SC spectrum increases as $PO_4^{3-} < SO_4^{2-} < NO_3^- < Br^- < I^-$ and concludes that the hydrogen bonding of water occurs in the hydration shell of PO_4^{3-} anion rather than in SO_4^{2-}.

3.1.2. Evaluation of the Binary Parameters and Activity Coefficients. The specific interaction approach to describe electrolyte solutions at high concentration introduced by Pitzer[52,53] represents a significant advance in physical chemistry that has facilitated the construction of accurate thermodynamic models. The equation of osmotic coefficient for electrolyte is given by eq 2:

$$\phi - 1 = |z_M z_X| f^\phi + m\left(\frac{2\nu_M\nu_X}{\nu}\right)B_{MX}^\phi + m^2\left(2\frac{(\nu_M\nu_X)^{3/2}}{\nu}\right)C_{MX}^\phi$$

$$(2)$$

where f^ϕ is the long-range electrostatic term, and the second virial coefficient B^ϕ is given by eq 3,

$$B_{MX}^\phi = \beta^{(0)} + \beta^{(1)} \exp(-\alpha I^{1/2})$$

$$(3)$$

where $\alpha = 2.0$ kg$^{1/2}$·mol$^{-1/2}$ and $b = 1.2$ kg$^{1/2}$·mol$^{-1/2}$, respectively. I is the ionic strength. The ion interaction model gives the mean activity coefficients γ as

$$\ln \gamma = |z_M z_X| f^\gamma + m\left(\frac{2\nu_M\nu_X}{\nu}\right)B_{MX}^\gamma + m^2\left(2\frac{(\nu_M\nu_X)^{3/2}}{\nu}\right)C_{MX}^\gamma$$

$$(4)$$

f^γ is the long-range electrostatic term

B_{MX}^{γ} is defined as

$$B_{MX} = \beta_{MX}^{(0)} + \left(\frac{2\beta_{MX}^{(1)}}{\alpha^2 I^2}\right)[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})]$$

(5)

$Na_3PO_4-H_2O$ and $Na_2SO_4-H_2O$ are considered as binary solutions with 1−3 and 1−2 charge-types, respectively, that is, without considering formation of aqueous complexes. In constructing the model of the $Na_3PO_4(aq)$ and $Na_2SO_4(aq)$ systems from (298.15 to 353.15) K, single electrolyte ion-interaction parameters ($\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ) are adjusted to fit the obtained osmotic coefficients (Table 2). It was found, that the standard for 1−3 and 1−2 charge-types of electrolytes approach with three $\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ single electrolyte ion-interaction parameters for $Na_3PO_4(aq)$ and $Na_2SO_4(aq)$, respectively, give a good agreement with osmotic coefficients data. The parameters and the standard deviation of fit $\sigma(\phi)$ are given in Table 3.

Table 3. Ion Interaction Parameters $\beta^{(0)}$, $\beta^{(1)}$, $C^{(\phi)}$ of Binary Systems $Na_2SO_4-H_2O$ and $Na_3PO_4-H_2O$ in the Temperature Range from (298.15 to 353.15) K and the Saturated Molality $m_{s(exp)}$[a]

T	$\beta^{(0)}$	$\beta^{(1)}$	$C^{(\phi)}$		
K	kg·mol^{-1}	kg·mol^{-1}	kg^2·mol^{-2}	σ_ϕ	$m_{s(exp)}$
		$Na_2SO_4-H_2O$			
298.15	0.0394 (0.0037)	0.969 (0.047)	−0.00175 (0.00011)	0.0006	1.97
313.15	0.0394 (0.0072)	0.764 (0.069)	0.00082 (0.00007)	0.0005	3.40
333.15	0.0762 (0.0034)	0.128 (0.022)	0.00588 (0.00014)	0.0019	3.20
353.15	0.0780 (0.0060)	0.455 (0.007)	−0.00622 (0.00015)	0.0003	3.00
		$Na_3PO_4-H_2O$			
298.15[b]	0.1759 (0.0016)	3.907 (0.023)	−0.05230 (0.00260)	0.0007	0.68
313.15	0.1518 (0.0031)	4.411 (0.074)	−0.02550 (0.00310)	0.0005	1.10
333.15	0.1320 (0.0010)	5.008 (0.035)	−0.01150 (0.00011)	0.002	2.80
353.15	0.0983 (0.0001)	6.456 (0.005)	−0.00365 (0.00001)	0.006	9.00

[a]Standard uncertainty of temperature $u(T) = 0.1$ K, and molality $u(m_{s(exp)}) = 0.01$ mol·kg^{-1}. The expanded uncertainty U (0.95 level of confidence) of parameters is calculated for each temperature and it is given in brackets. $\sigma_\phi = ((\sum(\phi_{obs} - \phi_{th})^2)/(N - 1))^{1/2}$ where N is the number of experimental data points. [b]Reference 40.

The expanded uncertainty U (0.95 level of confidence) of parameters is also calculated for each temperature and it is given in brackets.

Using the ion interaction parameters, the solute activity coefficients are calculated by eq 4 and given in Table 2. The predicted mean activity coefficients of $Na_3PO_4(aq)$ and $Na_2SO_4(aq)$ as a function of molality at various temperatures ranging from $T = (298.15$ to 353.15) K are also shown in Figure 1.

3.1.3. Excess Gibbs Energy. The thermodynamic properties of aqueous solutions at different temperatures are of major importance in many areas and industrial processes.[54,55] In addition to the osmotic and activity coefficients, there is signifiant interest in the excess Gibbs energy of Na_3PO_4 and Na_2SO_4 aqueous solutions. Nevertheless, the thermodynamic functions

of phosphate, sulfate aqueous solutions are poorly given at different temperatures. The osmotic and activity coefficients can be used to evaluate the excess Gibbs energy G^{ex} of the solution by eq 6:

$$G^{ex} = \nu m R T (1 - \phi + \ln\gamma)$$

(6)

The excess Gibbs energies of $Na_3PO_4(aq)$ or $Na_2SO_4(aq)$ solutions were calculated at various temperatures from (298.15 to 353.15) K and presented in Figure 3. G^{ex} against molality is
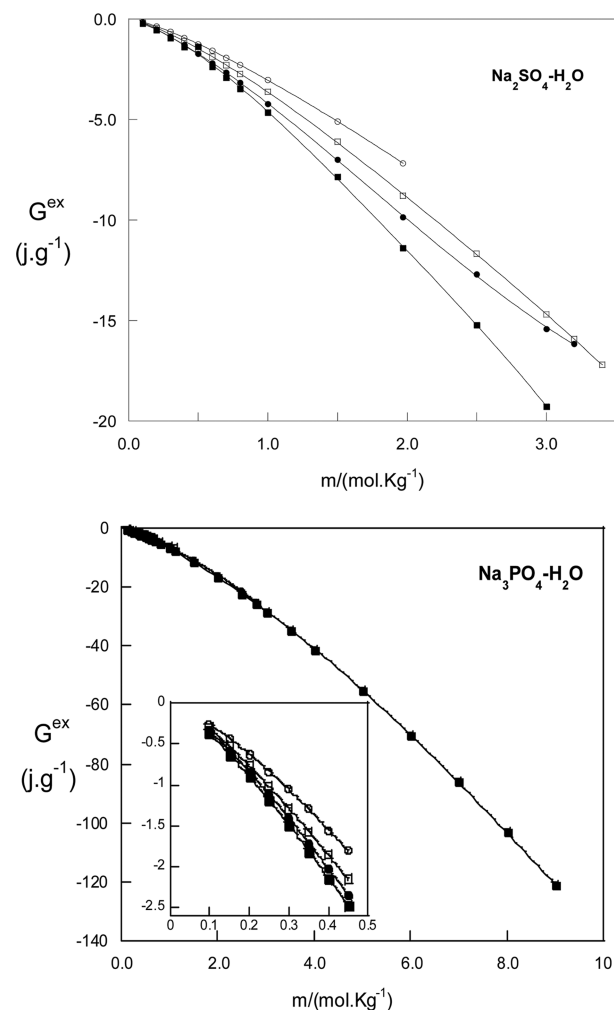
Figure 3. Excess Gibbs energy G^{ex} of $Na_2SO_4(aq)$ and $Na_3PO_4(aq)$ as a function of molality m at different temperatures: (○) 298.15 K; (□) 313.15 K; (●) 333.15 K; (■) 353.15 K.

almost similar in the temperature range. However, the difference appears in concentrated solutions. The lowest G^{ex} is given at $T = 353.15$ K, indicating that the solution becomes relatively more stable at elevated temperature. The values are generally negative $G^{ex} < 0$ in the systems present and then relatively stable at high concentration and elevated temperature. The comparison of the excess Gibbs energy for the binary systems indicates that the phosphate aqueous solutions become relatively more stable than those of sulfate over the ranges of molality and temperature from (298.15 to 353.15) K, $G^{ex}_{(Na_3PO_4)} < G^{ex}_{(Na_2SO_4)}$ (Figure 4). This stability is favored at elevated temperature. This phenomenon can be explained by an ionic association and formation of ion pairing and/or complexes in aqueous solutions.
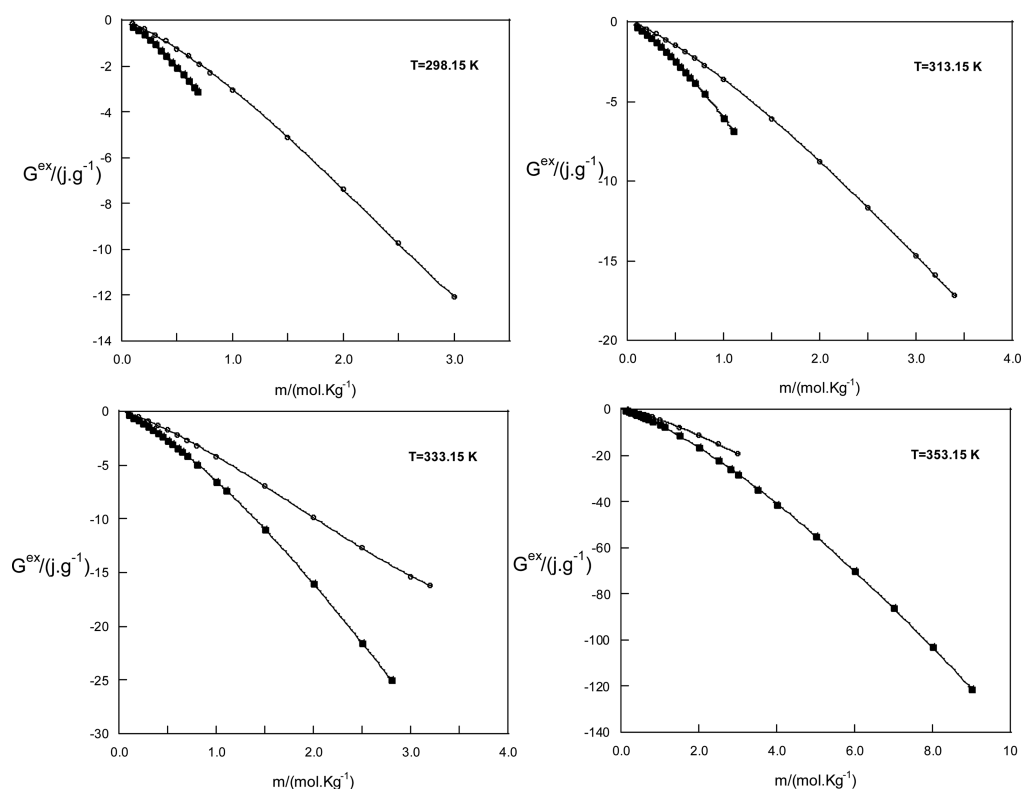
Figure 4. Comparison of excess Gibbs energy G^{ex} as a function of molality m of the binary solutions $Na_2SO_4(aq)$ and $Na_3PO_4(aq)$ for each temperature: (■) $Na_3PO_4(aq)$ and (○) $Na_2SO_4(aq)$.

3.1.4. Solubility. In the saturated solutions, the solubility of a hydrated salt is evaluated from the equilibrium constant of the hydrated salt and the activity coefficients of all the electrolytes. The solubility of a mineral system studied at different temperatures is determined on thermodynamic considerations based on the approach of the ion interaction model.[4,25,56−59]

According to the binary experimental data of $Na_3PO_4−H_2O$ and $Na_2SO_4−H_2O$, water activity and mineral solubility $m_{s(exp)}$ are directly derived from experimental measurements. The solubility of the binary systems is determined and tabulated (Table 4). From these data, $Na_2SO_4·10H_2O$ is in a stable phase at 298.15 K, where it undergoes a phase transformation to anhydrous $Na_2SO_4{}_{(Cr)}$ from (313.15 to 353.15) K. For phosphate, $Na_3PO_4·$ $12H_2O·^1/_4NaOH$ is a stable phase from (298.15 to 313.15) K; it crystallizes in $Na_3PO_4·8H_2O$ at 333.15 K and transforms to $Na_3PO_4·6H_2O$ at 353.15 K.[60−62]

The solubility modeling approach based on ion interaction equations is also employed. The standard for (1−3 or 1−2) charge type respectively for $Na_3PO_4(aq)$ or $Na_2SO_4(aq)$ of electrolytes approach with three $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} single electrolyte ion-interaction parameters gives a very good agreement with the osmotic coefficients data for unsaturated solutions, and with phosphate or sulfate salts equilibrium solubility data, used in parametrization. As a test of the solid−liquid equilibria, the model prediction is compared with the experimental solubility isotherms. Experimental, calculated, and reference molalities m_s for the saturated binary solutions were given in Table 4 for each temperature. The good agreement obtained, between the experimental and calculated values of m_s, shows the consistency of the binary systems $Na_3PO_4−H_2O$, $Na_2SO_4−H_2O$ model within the temperature range from T = (298.15 to 353.15) K. For $Na_2SO_4(aq)$, the molalities of saturated solutions m_s are

Table 4. Logarithm of the Thermodynamic Solubility Product, $\ln K^{\circ}_{sp}$; Phase Solid; Experimental $m_{s(exp)}$, Calculated $m_{s(cal)}$ and Literature $m_{s(cal)ref}$ of Saturated Molality of $Na_2SO_4−H_2O$ and $Na_3PO_4−H_2O$ at Different Temperatures Ranging from (298.15 to 353.15) K

		mol·kg^{-1} (H_2O)			
T/K	phase solid	$m_{s\,(exp)}$	$m_{s\,(cal)}$	$m_{s\,(cal)ref}$	$\ln K^{\circ}_{sp(cal)}$
		$Na_2SO_4−H_2O$			
298.15	$Na_2SO_4·10H_2O^a$	1.97	1.999	1.9783^c 1.934^d	−2.790
313.15	Na_2SO_4 anhydre^a	3.40	3.412	3.3666^c	−1.751
333.15		3.20	3.226	3.1482^c	−1.588
353.15		3.00	2.996	3.0201^c	−2.967
		$Na_3PO_4−H_2O$			
298.15	$Na_3PO_4·12H_2O·$ $^1/_4NaOH^{a,b}$	0.68	0.681		−6.0990
313.15		1.10	1.102		−17.0380
333.15	$Na_3PO_4·8H_2O^{a,b}$	2.80	2.877		−8.4129
353.15	$Na_3PO_4·6H_2O^{b,c}$	9.00	9.504		−10.3178

^{a}Reference 60. ^{b}Reference 61. ^{c}Reference 62. ^{d}Reference 63 standard uncertainty of molality is $u(m_{s(exp)})$ = 0.01 mol·kg^{-1}.

compared with the available literature data $(m_{s(ref)})$; good agreement is observed except at T = 298.15K.[63]

Thermodynamic Solubility Product. From water activity measurements in the molality range, the solute activity coefficients were calculated using the ion interaction model for the binary aqueous solutions. The Pitzer−based model constructed here was used to calculate the thermodynamic solubility product (given in $\ln K^{\circ}_{sp}$) of phosphate or sulfate salts within the temperature range from T = 298.15 K to T = 353.15 K (Table 4). The calculated values of $\ln K^{\circ}_{sp}$ were determined for the sulfates of $Na_2SO_4·10H_2O(cr)$, $Na_2SO_4(cr)$ and phosphates of

Table 5. Water Activity and Osmotic Coefficient ϕ of the Solvent of Ternary System $\{y\text{Na}_3\text{PO}_4 + (1 - y)\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}\}$ at Total Molality m for Different Ionic-Strength Fractions (y) of Na_3PO_4 at Various Temperatures (298.15 to 353.15) K and Pressure ($P = 0.1$ MPa)[a]

mol·kg^{-1}(H$_2$O)			T/K = 298.15		T/K = 313.15		T/K = 333.15		T/K = 353.15K	
m	$m_{\text{Na}_3\text{PO}_4}$	$m_{\text{Na}_2\text{SO}_4}$	a_w	ϕ	a_w	ϕ	a_w	ϕ	a_w	ϕ
					$y = 0.20$					
0.10	0.011	0.089	0.9956	0.779	0.9957	0.769	0.9959	0.727	0.9959	0.736
0.20	0.022	0.178	0.9918	0.738	0.9919	0.728	0.9924	0.680	0.9923	0.686
0.30	0.033	0.267	0.9881	0.715	0.9883	0.699	0.9890	0.656	0.9890	0.658
0.40	0.045	0.356	0.9846	0.691	0.9849	0.681	0.9858	0.640	0.9858	0.638
0.50	0.056	0.445	0.9813	0.675	0.9816	0.663	0.9825	0.631	0.9826	0.625
1.00	0.111	0.890	0.9656	0.625	0.9659	0.620	0.9657	0.622	0.9674	0.591
1.50	0.167	1.335	0.9507	0.602	0.9502	0.608	0.9470	0.648	0.9520	0.585
1.70	0.189	1.513	0.9447	0.597	0.9440	0.605	0.9382	0.667	0.9440	0.583
2.00	0.223	1.780			0.9340	0.609	0.9253	0.693	0.9356	0.594
3.00	0.334	2.670			0.8995	0.630	0.8719	0.815	0.9036	0.603
3.50	0.389	3.115			0.8818	0.641	0.8399	0.889	0.8877	0.608
4.00	0.445	3.560							0.8720	0.611
					$y = 0.50$					
0.10	0.033	0.067	0.9954	0.753	0.9955	0.748	0.9957	0.712	0.9957	0.722
0.20	0.067	0.133	0.9915	0.709	0.9916	0.702	0.9920	0.666	0.9919	0.675
0.30	0.100	0.200	0.9878	0.683	0.9880	0.672	0.9886	0.637	0.9885	0.650
0.40	0.133	0.267	0.9844	0.657	0.9845	0.649	0.9853	0.617	0.9844	0.626
0.50	0.167	0.333	0.9810	0.638	0.9812	0.631	0.9817	0.613	0.9822	0.597
1.00	0.333	0.667	0.9658	0.580	0.9658	0.580	0.9658	0.579	0.9679	0.543
1.40	0.467	0.933	0.9547	0.551	0.9540	0.566	0.9516	0.591	0.9562	0.527
1.50	0.500	1.000			0.9504	0.565	0.9476	0.598	0.9537	0.526
2.00	0.667	1.333			0.9352	0.558	0.9267	0.634	0.9386	0.528
2.50	0.833	1.667			0.9199	0.556	0.9033	0.614	0.9224	0.532
3.00	1.000	2.000					0.8756	0.737	0.9068	0.543
4.00	1.333	2.667					0.8130	0.862	0.8735	0.563
					$y = 0.80$					
0.10	0.067	0.033	0.9953	0.715	0.9953	0.713	0.9955	0.689	0.9954	0.705
0.20	0.133	0.067	0.9912	0.666	0.9913	0.664	0.9916	0.637	0.9915	0.649
0.30	0.200	0.100	0.9875	0.635	0.9876	0.632	0.9882	0.600	0.9881	0.604
0.40	0.267	0.133	0.9842	0.605	0.9842	0.602	0.9850	0.572	0.9851	0.569
0.50	0.333	0.167	0.9809	0.583	0.9810	0.580	0.9819	0.552	0.9824	0.539
1.00	0.667	0.333			0.9662	0.520	0.9671	0.506	0.9699	0.462
1.50	1.000	0.500			0.9519	0.498	0.9505	0.513	0.9566	0.448
2.00	1.333	0.667			0.9384	0.481	0.9315	0.538	0.9427	0.447
3.00	2.000	1.000					0.8873	0.603	0.9094	0.479
3.50	2.333	1.167					0.8651	0.627	0.8922	0.497
4.00	2.667	1.333							0.8723	0.517
4.50	3.000	1.500							0.8551	0.525

[a]Standard uncertainty of temperature is $u(T) = 0.1$ K and molality is $u(m) = 0.01$ mol·kg^{-1}. The relative standard uncertainty is $u_r(a_w) = 0.0002$ for $a_w > 0.97$; $u_r(a_w) = 0.0005$ for $0.97 > a_w > 0.95$; $u_r(a_w) = 0.0009$ for $0.95 > a_w > 0.90$ and $u_r(a_w) = 0.002$ for $a_w < 0.90$. Standard uncertainty of osmotic coefficient ϕ is estimated at $u(\phi) = 0.005$. Each point is the average of 8 to 10 series of experiments.

Na$_3$PO$_4$·12H$_2$O·$^1/_4$NaOH; Na$_3$PO$_4$·8H$_2$O and Na$_3$PO$_4$·6H$_2$O. If the literature data exist, the comparison was made, in this case specially at 298.15 K for ln K_{sp}° of Na$_2$SO$_4$·10H$_2$O(cr), a slight difference is observed.[63]

3.2. Ternary System $\{y\text{Na}_3\text{PO}_4 + (1 - y)\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}\}$. The thermodynamic properties of mixing of aqueous solutions with salts having a common cation or anion continue to be interesting. The properties of the aqueous systems Na$_3$PO$_4$ + Na$_2$SO$_4$ + H$_2$O were measured using the hygrometric method in the temperature range $T = (298.15$ to $353.15)$ K, in which this ternary has not been extensively studied. The mixed aqueous electrolytes of sodium phosphate and sulfate $\{y\text{Na}_3\text{PO}_4 + (1 - y)\text{Na}_2\text{SO}_4\}(\text{aq})$ were investigated at a total molality from 0.10 mol·kg^{-1} to saturation for different ionic-strength fractions (y) of Na$_3$PO$_4$ with $y = 0.20$, 0.50, and 0.80.

3.2. 1. Water Activity and the Osmotic Coefficient. The water activities for $\{y\text{Na}_3\text{PO}_4 + (1 - y)\text{Na}_2\text{SO}_4\}(\text{aq})$ were measured at total molality from 0.10 mol·kg^{-1} to saturation for different ionic-strength fractions (y) of Na$_3$PO$_4$ $y = I_{\text{Na}_3\text{PO}_4}/(I_{\text{Na}_3\text{PO}_4} + I_{\text{Na}_2\text{SO}_4})$ with $y = 0.20$, 0.50, and 0.80, with the limiting cases of y corresponding to the pure electrolytes $y = 0$ and $y = 1$. The measurements of water activity at various temperatures $T = (298.15$ to $353.15)$ K are reported in Table 5 and presented in Figure 5. From the water activities, the osmotic coefficients were also evaluated for these solutions. A comparison of the relative magnitude of these water activities, Figure 5, shows that the curves are similar at $T = 298.15$ K and 313.15 K. Therefore, the anion effect of the added electrolyte does not cause significant change in the structure of the solution in the immediate vicinity, where its size and nature allow fitting in without creating
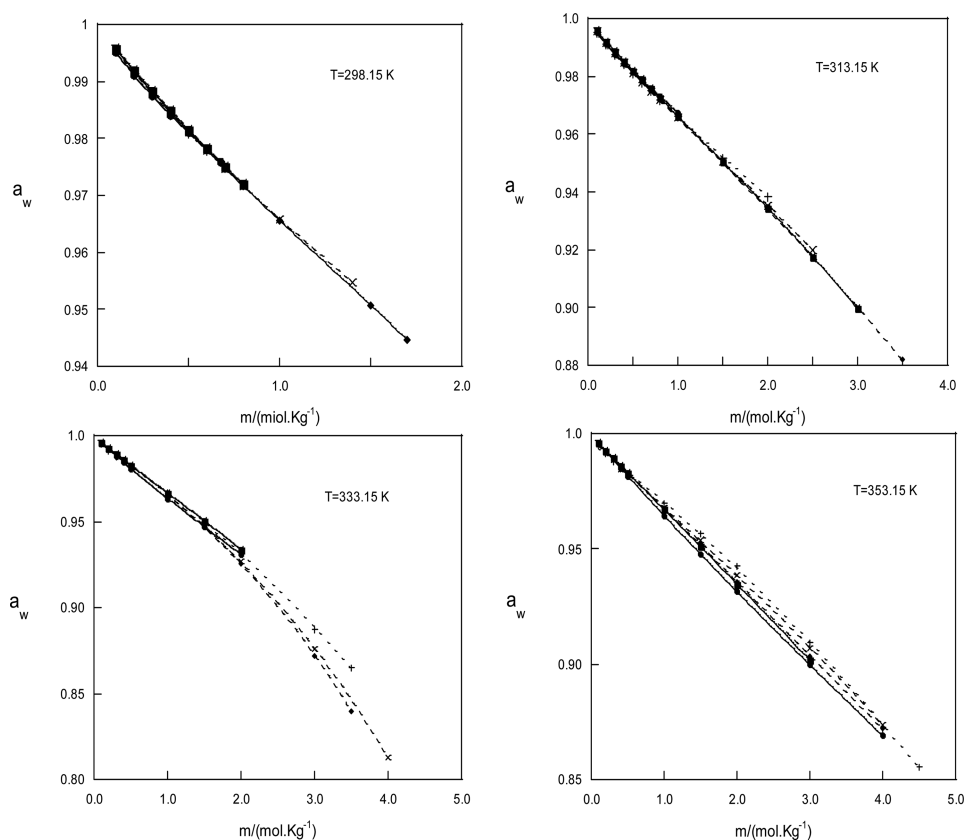
Figure 5. Water activities a_w of aqueous solutions $\{yNa_3PO_4 + (1 - y)Na_2SO_4\}(aq)$ as a function of molality at various temperatures from (298.15 to 353.15) K for different ionic-strength fractions (y) of Na_3PO_4: ■, $y = 0.00$; ♦, $y = 0.20$; ×, $y = 0.50$; +, $y = 0.80$; ●, $y = 1.00$.

new constraints. Thus, the water molecules retain the same ionic environment, and therefore are subject to the same electrostatic effect. The added solute Na_2SO_4 to the solution of $Na_3PO_4(aq)$ (in which $Na_3PO_4(aq)$ is considered as supporting electrolyte) increases the water activity of the mixture, which becomes higher than that of the $Na_3PO_4(aq)$.

3.2.2. Determination of the Activity Coefficients and Excess Gibbs Energy. The ionic interaction model[52,53,64] is used to calculate the thermodynamic properties of mixed-electrolyte solutions. This model requires parameters estimated from common-ion solutions in order to characterize binary interactions among different ions of the same sign and ternary interactions between different ions not all of the same sign in a mixed electrolyte solution. The osmotic coefficients of a mixed solution of two salts Na_2SO_4 and Na_3PO_4 with a common cation are given by eq 7:

$$\phi - 1 = \left(\sum_i m_i\right)^{-1}\left\{2If^\phi + 2\sum_c\sum_a m_c m_a\left[B_{ca}^\phi + \frac{(\sum m_z)}{(z_c z_a)^{1/2}}C_{ca}^\phi\right]\right.$$
$$+ \sum_c\sum_{c'} m_c m_{c'}[\theta_{cc'} + I\theta_{cc'}' + \sum_a m_a \psi_{cc'a}]$$
$$\left. + \sum_a\sum_{a'} m_a m_{a'}[\theta_{aa'} + I\theta_{aa'}' + \sum_c m_c \psi_{caa'}]\right\} \quad (7)$$

where θ and θ' ($\theta_{PO_4SO_4}$) are the binary mixing parameters for mixing unlike ions of the same sign and ψ ($\psi_{NaPO_4SO_4}$) is a ternary parameter for mixing two unlike ions of the same sign with a third ion of the opposite sign

The second virial coefficient B^ϕ of the ions is defined as a function of the ion-interaction parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ

which are functions of temperature and pressure (Table 3). The activity coefficient γ_{MX} of MX ($\gamma_{Na_2SO_4}$; $\gamma_{Na_3PO_4}$) in a common cation mixture is given by eq 8:

$$\ln \gamma_{MX} = |z_M z_X|f^\gamma + \left(2\frac{\nu_M}{\nu}\right)\sum_a m_a$$
$$\times\left[B_{Ma} + (\sum m_z)C_{Ma} + \left(\frac{\nu_X}{\nu_M}\right)\theta_{Xa}\right]$$
$$+ \left(2\frac{\nu_X}{\nu}\right)\sum_c m_c\left[B_{cX} + (\sum m_z)C_{cX}\right.$$
$$\left. + \left(\frac{\nu_M}{\nu_X}\right)\theta_{Mc}\right] + \sum_c\sum_a m_c m_a\{|z_M z_X|B_{ca}'$$
$$+ \nu^{-1}[2\nu_M z_M C_{ca} + \nu_M \psi_{Mca} + \nu_X \psi_{caX}]\}$$
$$+ \frac{1}{2}\sum_c\sum_{c'} m_c m_{c'}\left[\left(\frac{\nu_X}{\nu}\right)\psi_{cc'X} + |z_M z_X|\theta_{cc'}'\right]$$
$$+ \frac{1}{2}\sum_a\sum_{a'} m_a m_{a'}\left[\left(\frac{\nu_M}{\nu}\right)\psi_{Maa'} + |z_M z_X|\theta_{aa'}'\right] \quad (8)$$

Evaluation of the Mixing Parameters for the System $\{yNa_3PO_4 + (1 - y)Na_2SO_4 + H_2O\}$. The experimental water activities are used to calculate the osmotic coefficients at different ionic-strength fractions y. The mixing ionic parameters $\theta_{PO_4SO_4}$ and $\psi_{NaPO_4SO_4}$ are not given in the literature. These parameters are estimated by a graphical procedure which defines the quantity

**Table 6. Ion Interaction Parameters θ_{PO_4,SO_4} and $\psi_{NaPO_4SO_4}$ in the Ternary System $\{y\text{Na}_3\text{PO}_4 + (1-y)\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}\}$ at Various Temperatures from (298.15 to 353.15) K**

ternary system	T/K	θ_{MN}	ψ_{MNX}	$\sigma(\phi)$
$\{y\text{Na}_3\text{PO}_4 + (1-y)\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}\}$	298.15	−0.1141	0.0543	0.0042
	313.15	0.0835	−0.0103	0.0031
	333.15	0.0540	−0.0072	0.0057
	353.15	0.0593	−0.0054	0.0045
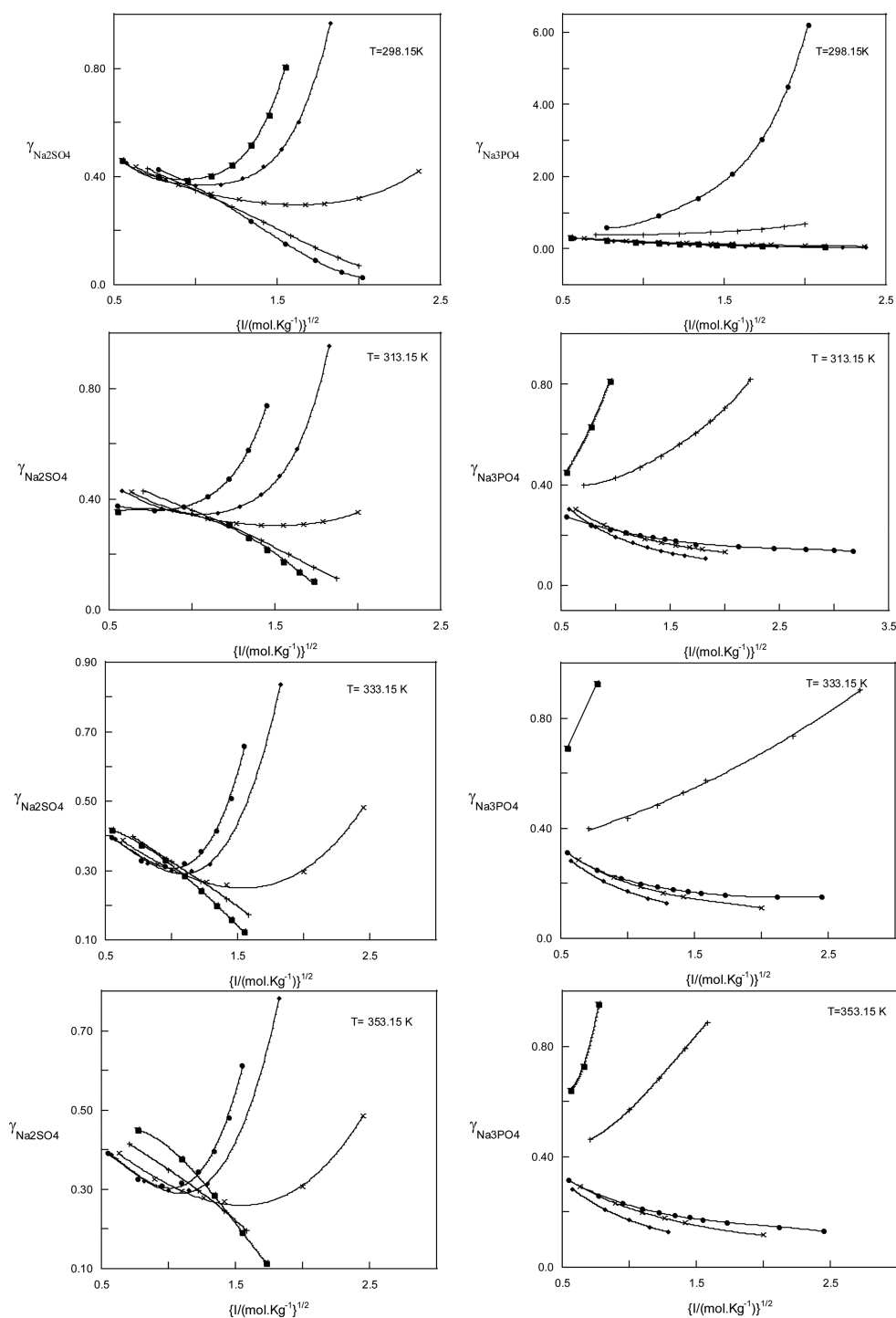
Figure 6. Activity coefficient $\gamma_{\text{Na}_3\text{PO}_4}$ and $\gamma_{\text{Na}_2\text{SO}_4}$ of $\{y\text{Na}_3\text{PO}_4 + (1-y)\text{Na}_2\text{SO}_4\}(\text{aq})$ as a function of square root of the ionic strength $I^{1/2}$ at various temperatures from (298.15 to 353.15) K and at different ionic-strength fractions (y) of Na$_3$PO$_4$: ■, $y = 0.00$; ♦, $y = 0.20$; ✕, $y = 0.50$; +, $y = 0.80$; ●, $y = 1.00$.
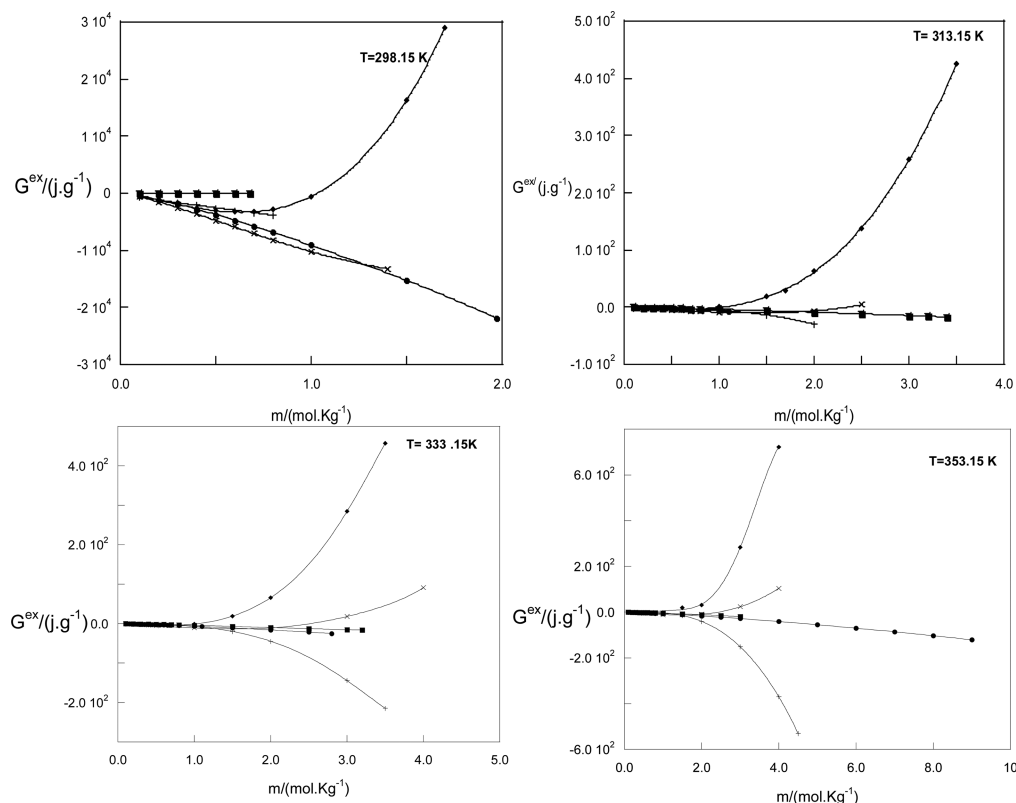
Figure 7. Excess Gibbs energy of $\{y\text{Na}_3\text{PO}_4 + (1-y)\text{Na}_2\text{SO}_4\}(\text{aq})$ against total molality m at different temperatures and at different ionic-strength fractions (y) of Na_3PO_4: ■, $y = 0.00$; ♦, $y = 0.20$; ×, $y = 0.50$; +, $y = 0.80$; ●, $y = 1.00$.

$\Delta\phi$ eq 9 as the difference between the experimental values ϕ_{exp} and that calculated from eq 7,

$$\left(\frac{\sum m_i}{2m_{\text{Na}_3\text{PO}_4}m_{\text{Na}_2\text{SO}_4}}\right)\Delta\phi = \left(\frac{4m_{\text{Na}_3\text{PO}_4} + 3m_{\text{Na}_2\text{SO}_4}}{2m_{\text{Na}_3\text{PO}_4}m_{\text{Na}_2\text{SO}_4}}\right)\Delta\phi$$

$$= \theta_{\text{PO}_4\text{SO}_4} + \psi_{\text{PO}_4\text{SO}_4}m_{\text{Na}} \qquad (9)$$

with $m_{\text{Na}} = 3m_{\text{Na}_3\text{PO}_4} + 2m_{\text{Na}_2\text{SO}_4}$.

So that a graphical procedure should give a straight line with intercept $\theta_{\text{PO}_4\text{SO}_4}$ and slope $\psi_{\text{NaPO}_4\text{SO}_4}$. The values of these parameters at various temperatures ranging from (298.15 to 353.15) K are listed in Table 6.

Activity Coefficients and Excess Gibbs Energy. The activity coefficients $\gamma_{\text{Na}_2\text{SO}_4}$ and $\gamma_{\text{Na}_3\text{PO}_4}$ in the ternary system $\{y\text{Na}_3\text{PO}_4 + (1-y)\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}\}$ were calculated at total molality from dilution to saturation for different ionic-strength fractions (y) of Na_3PO_4 with $y = 0.20$, 0.50, and 0.80 using the obtained mixing parameters at different temperatures from (298.15 to 353.15) K (Figure 6). From the obtained osmotic and activity coefficients data, the excess Gibbs energy for $\text{Na}_3\text{PO}_4 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ was determined eq 10) at various temperatures for different ionic-strength fractions y of Na_3PO_4 (Figure 7). The thermodynamic properties of the ternary aqueous systems of phosphate and sulfate with sodium are compared, and the comparison shows that the type of anion solute PO_4 or SO_4 influences the hydration in the mixed aqueous solutions.

$$G^{\text{ex}} = RT \sum_i m_i\nu_i(1 - \phi + \ln\gamma_i) \qquad (10)$$

4. CONCLUSION

The thermodynamic properties of the aqueous solutions of sulfate and phosphate and their mixtures with a common cation

were studied experimentally in the temperature range from (298.15 to 353.15) K, using the hygrometric method. The constructed model was developed based on ion interaction to study the binary systems $\text{Na}_3\text{PO}_4(\text{aq})$ and $\text{Na}_2\text{SO}_4(\text{aq})$, and ternary aqueous solutions $\{y\text{Na}_3\text{PO}_4 + (1-y)\text{Na}_2\text{SO}_4\}(\text{aq})$ for different ionic-strength fractions (y) of Na_3PO_4 with $y = 0.20$, 0.50, and 0.80 at various temperatures (298.15 to 353.15) K.

In constructing the model for the $\text{Na}_3\text{PO}_4(\text{aq})$ and $\text{Na}_2\text{SO}_4(\text{aq})$ systems from (298.15 to 353.15) K, single electrolyte parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ were adjusted to fit the obtained osmotic coefficients data. The standards of 1–3 and 1–2 charge-types respectively for $\text{Na}_3\text{PO}_4(\text{aq})$ and $\text{Na}_2\text{SO}_4(\text{aq})$ electrolytes approach with three $\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ single electrolyte ion-interaction parameters give a very good agreement with osmotic coefficients data for unsaturated solutions, with $\text{Na}_3\text{PO}_4(\text{s})$ and $\text{Na}_2\text{SO}_4(\text{s})$ equilibrium solubility data, used in parametrization.

The mineral solubility of the binary systems was determined at various temperatures ranging from (298.15 to 353.15) K and the excess Gibbs energies were calculated from dilute up to saturated solution. The comparison of $\text{Na}_3\text{PO}_4(\text{aq})$ and $\text{Na}_2\text{SO}_4(\text{aq})$ behaviors in aqueous solutions shows that the hydration is affected by the nature of anion solute (PO_4 or SO_4); and the hydration effect of PO_4 is higher than SO_4.

The water activities of the ternary system and related properties such as osmotic and activity coefficients were performed at various temperatures ranging from (298.15 to 353.15) K. The osmotic coefficients data were used to evaluate the activity coefficients using the mixing parameters $\theta_{\text{PO}_4\text{SO}_4}$ and $\psi_{\text{NaPO}_4\text{SO}_4}$. The excess Gibbs energies of $\{y\text{Na}_3\text{PO}_4 + (1-y)\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}\}$ were also determined at various temperatures for different ionic-strength fractions y of Na_3PO_4 with $y = 0.20$, 0.50, and 0.80.

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