Apparent Molar Volumes and Standard Partial Molar Volumes of Aqueous Sodium Phosphate Salts at Elevated Temperatures

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Densities and apparent molar volumes of aqueous NaH_2PO_4 (0.1 to 2.1) mol·kg^{-1}, Na_2HPO_4 (0.1 to 0.5) mol·kg^{-1} and Na_3PO_4 (0.4 to 0.6) mol·kg^{-1} have been determined using a platinum vibrating tube densimeter at temperatures from 473 K to 598 K, 473 K to 570 K, and 373 K to 497 K, respectively, and a pressure of 15 MPa. For the monosodium and disodium phosphate salts, the Pitzer ion-interaction model was used to extrapolate the apparent molar volumes to infinite dilution and to obtain standard partial molar volumes, $V°$, of NaH_2PO_4(aq) and Na_2HPO_4(aq). These new results show that predicted values from the Helgeson−Kirkham−Flowers model overestimate $V°$ for these two species. For the monosodium salt, the difference ranged from 5 cm^3·mol^{-1} at 473 K to 24 cm^3·mol^{-1} at 573 K, and for the disodium salt, the difference was 6 cm^3·mol^{-1} at 473 K and 16 cm^3·mol^{-1} at 570 K. The values for disodium phosphate show evidence of significant contributions from an ion pair, probably $NaHPO_4^-$(aq). The apparent molar volumes of Na_3PO_4(aq) could only be obtained over a narrow range of concentration due to hydrolysis, and consequently it was not possible to determine $V°$ of the species PO_4^{3-}(aq) from their concentration dependence.

Introduction

Dilute solutions of sodium phosphate are used to control pH and to control scale formation in the high pressure boilers of thermal power stations. The operating temperatures encountered at full load may be as high as 630 K, and even higher temperatures may be encountered in localized "hot spots" under deposits or in crevices. Chemical equilibrium models are used to predict the occurrence of phosphate precipitation at local sites and to optimize boiler-water chemistry. However, only a few experimental measurements of the standard state and excess properties of phosphate solutions have been reported at temperatures above 373 K.

Mesmer and Baes[1] have determined equilibrium quotients for the first and second neutralization reactions of aqueous phosphoric acid at temperatures up to 573.15 K and ionic strength up to 1 mol·kg^{-1}, and a few values were reported for the third neutralization reaction up to 423.15 K. Osmotic and activity coefficients have been measured by isopiestic methods for H_3PO_4(aq) at temperatures between 383.15 K and 523.15 K by Holmes and Mesmer[2] and for aqueous NaH_2PO_4, KH_2PO_4, Na_2HPO_4, and K_2HPO_4 between 383.15 K and 498.15 K by Holmes et al.[3] The thermodynamic properties of aqueous Na_3PO_4 and phase equilibria of alkaline Na_3PO_4 solutions at temperatures up to 373.15 K have been modeled by Weber et al.[4]

Standard partial molar volumes, $V°$, and standard heat capacities, $C_p°$, are important in this context because they can be used to fit parameters for semiempirical "equations of state" [5–7] which are used to predict equilibrium constants at elevated temperatures and pressures. Values of $V°$ and $C_p°$ for H_3PO_4(aq) have been determined up to 573.15 K and at pressures up to 28 MPa.[8] However, with the exception of some experimental densities for concentrated solutions by Söhnel et al.[9] at temperatures up 353.15 K, the apparent and standard partial molar volumes and heat capacities for the sodium salts of phosphoric acid, NaH_2PO_4(aq), Na_2HPO_4(aq), and Na_3PO_4(aq) have not been measured at temperatures above 298.15 K.[10–12]

The objective of this study was to address this shortfall, by determining the partial molar volumes of the aqueous phosphate ions under steam-generator operating conditions. In this paper, we report the first experimental values for the apparent and standard partial volumes of NaH_2PO_4(aq), Na_2HPO_4(aq) up to temperatures of 598 K, and 570 K, respectively and apparent molar volumes of Na_3PO_4(aq) up to 497 K.

Experimental Methods

Stock solutions of mono- and disodium salts were prepared by dissolving NaH_2PO_4(s) (Aldrich ReagentPlus, 99 %) and Na_2HPO_4(s) (Sigma-Aldrich ACS, ≥ 99.0 %), respectively, in Milli-Q water (18 MΩ·cm). The molalities of the stock solutions were determined to be (2.098 ± 0.004) mol·kg^{-1} NaH_2PO_4(aq) and (0.4964 ± 0.0006) mol·kg^{-1} Na_2HPO_4(aq) by titration in triplicate against secondary standard solutions of NaOH(aq) and HCl(aq), respectively. The reported uncertainty limits correspond to the standard deviation of the mean values of the three titrations. The trisodium phosphate stock solution was prepared by adding a stoichiometric amount of Na_2HPO_4(s) (Aldrich ReagentPlus, 99 %), dried at 423 K for one week, to a (0.6219 ± 0.0001) mol·kg^{-1} solution of NaOH(aq). Alkaline solutions were prepared and kept under an argon atmosphere to avoid the presence of dissolved CO_2. After accounting for the amount of water of neutralization, the molality of the stock solution was calculated to be 0.6173 mol·kg^{-1} Na_3PO_4(aq). All NaOH(aq) solutions were prepared by dilution of a 50 % (w/w) carbonate-free NaOH solution (Fisher Scientific) with Milli-Q water then standardized by titrating in triplicate against potassium hydrogen

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10.1021/je700764h CCC: $40.75

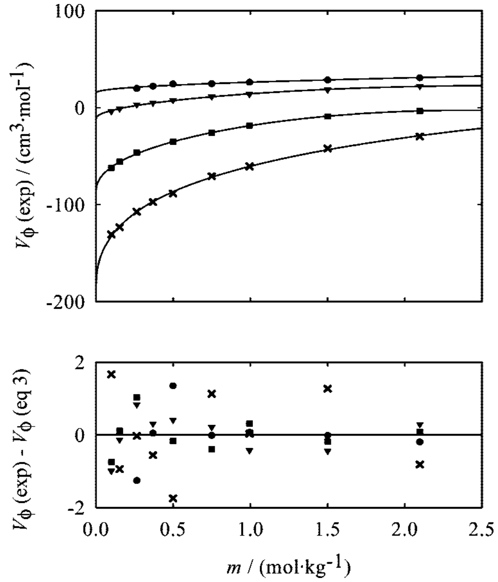

Figure 1. Apparent molar volumes of NaH_2PO_4(aq) at $p = 15$ MPa plotted against molality: •, 473 K; ▼, 523 K; ■, 573 K; ×, 598 K; —, isothermal fits (eq 3 and coefficients in Table 4).

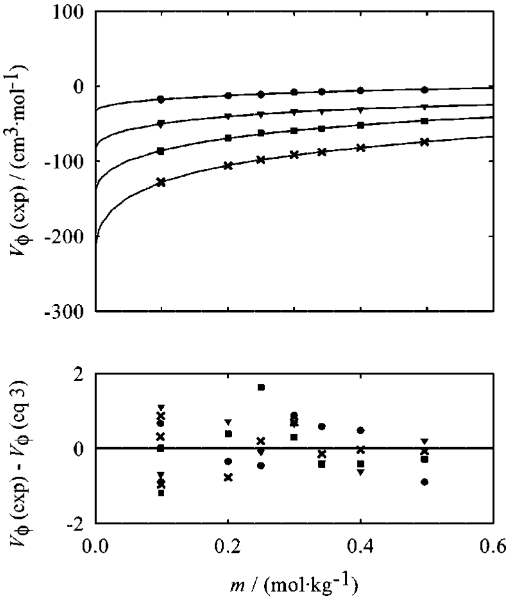

Figure 2. Apparent molar volumes of Na_2HPO_4(aq) at $p = 15$ MPa plotted against molality: •, 473 K; ▼, 523 K; ■, 548 K; ×, 570 K; —, isothermal fits (eq 3 and coefficients in Table 4).

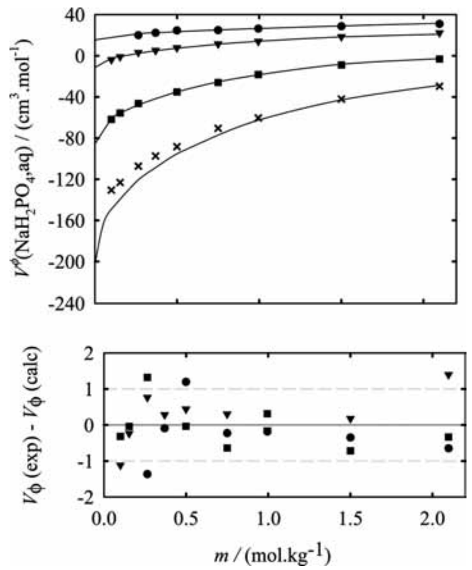

Figure 3. Apparent molar volumes of NaH_2PO_4(aq) at $p = 15$ MPa plotted against molality: •, 473 K; ▼, 523 K; ■, 573 K; ×, 598 K; —, global fit (eqs 5 to 7 and coefficients in Table 5).

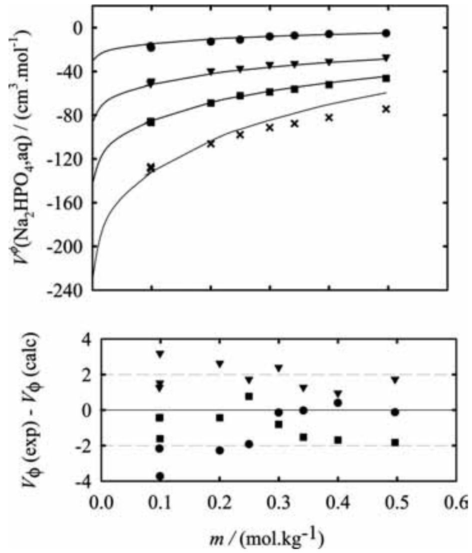

Figure 4. Apparent molar volumes of Na_2HPO_4(aq) at $p = 15$ MPa plotted against molality: •, 473 K; ▼, 523 K; ■, 548 K; ×, 570 K; —, global fit (eqs 5 to 7 and coefficients in Table 5).

phthalate (Fisher Scientific, ACS Grade, 99.99 %), which was dried for at least 48 h at 423 K. The masses of potassium hydrogen phthalate were not corrected for air buoyancy because the correction was negligible when compared with the standard deviation of the titrations. Standard solutions of HCl(aq) were made by diluting concentrated HCl(aq) (Fisher Scientific, Reagent ACS Grade) with Milli-Q water then titrating in triplicate against the standard solution of NaOH(aq). The reference solutions of NaCl(aq) for calibrating the densimeter were prepared by mass from NaCl(s) (Fisher Scientific, A.C.S.), which was dried for one week at 423.15 K. Deuterium oxide (D_2O), mole fraction 0.998 D, which was also used to calibrate the densimeter, was obtained from Ontario Power Generation (O.P.G.).

All titrations were done by mass using a Fisher Scientific Model 50 pH meter or a 794 Basic Titrino titrator. Nine solutions of the mono- and disodium phosphate salts and six solutions of the trisodium phosphate salt were prepared by dilution of their stock solution with Milli-Q water by mass. The molality of NaH_2PO_4(aq), Na_2HPO_4(aq), and Na_3PO_4(aq) ranged from (0.0999 to 2.098) mol·kg^{-1}, (0.0983 to 0.4964) mol·kg^{-1}, and (0.3986 to 0.6173) mol·kg^{-1}.

The relative densities of the electrolyte solutions were determined using the high-temperature platinum vibrating-tube flow densimeter described by Xiao et al.[13] and Clarke and Tremaine[14] from the expression

$$\rho - \rho_w^* = K(\tau^2 - \tau_w^*) \qquad (1)$$

Here, ρ and ρ_w^* are the densities of solution and pure water, respectively; τ and τ_w^* are the periods of oscillation associated with the solution and pure water, respectively; and K is a proportionality constant of the densimeter.[15] The proportionality constant K ($\approx 3.4 \cdot 10^5$ g·cm^{-3}s^{-2} at 200 °C) was calculated using eq 1 by comparing the resonance periods and densities

Table 1. Experimental Relative Densities, $\Delta\rho = (\rho - \rho_w^*)$, and Apparent Molar Volumes, V_ϕ (exp), for NaH_2PO_4 (aq) from T = 473 K to 598 K and p = 15 MPa[a]

T / K	P / MPa	m / $mol\cdot kg^{-1}$	$\Delta\rho$ / $g\cdot cm^{-3}$	ρ^b / $g\cdot cm^{-3}$	V_ϕ (exp) / $cm^3\cdot mol^{-1}$
T = (473.38 ± 0.02) K; p = (15.09 ± 0.02) MPa					
473.41	15.07	0.26427	0.02358	0.89792	19.96 ± 0.40
473.37	15.07	0.36934	0.03223	0.90660	22.24 ± 0.37
473.37	15.07	0.49927	0.04255	0.91692	24.57 ± 0.33
473.37	15.11	0.74990	0.06339	0.93779	24.85 ± 0.24
473.37	15.11	0.9946	0.08245	0.95685	26.30 ± 0.21
473.39	15.11	1.5007	0.12008	0.99446	28.64 ± 0.18
473.37	15.11	2.0977	0.16133	1.03573	30.92 ± 0.16
T =(522.85 ± 0.01) K; p = (15.01 ± 0.01) MPa					
522.84	14.99	0.09991	0.00999	0.82158	−3.87 ± 0.94
522.83	15.00	0.15312	0.01501	0.82662	−1.02 ± 0.78
522.87	15.00	0.26427	0.02517	0.83673	3.17 ± 0.52
522.85	15.01	0.36934	0.03467	0.84628	5.08 ± 0.41
522.86	15.01	0.49927	0.04594	0.85753	7.72 ± 0.33
522.83	15.02	0.74990	0.06689	0.87852	11.48 ± 0.29
522.85	15.02	0.9946	0.08677	0.89838	13.91 ± 0.27
522.85	15.03	1.5007	0.12507	0.93670	18.48 ± 0.22
522.86	15.03	2.0977	0.16719	0.97880	22.27 ± 0.19
T = (572.93 ± 0.03) K; p = (15.02 ± 0.06) MPa					
572.95	14.96	0.09991	0.01201	0.73802	−61.85 ± 0.61
572.92	15.08	0.15312	0.01795	0.74425	−55.68 ± 0.53
572.92	14.97	0.26427	0.02975	0.75583	−46.38 ± 0.46
572.90	14.98	0.49927	0.05344	0.77958	−35.18 ± 0.39
572.97	15.10	0.74990	0.07670	0.80292	−25.98 ± 0.33
572.91	14.99	0.9946	0.09751	0.82366	−18.26 ± 0.31
572.97	15.12	1.5007	0.13921	0.86550	−8.94 ± 0.26
572.92	15.00	2.0977	0.18719	0.91333	−3.17 ± 0.20
T = (597.71 ± 0.02) K; p = (15.16 ± 0.03) MPa					
597.69	15.18	0.09991	0.01392	0.68080	−130.55 ± 1.23
597.74	15.10	0.15312	0.02088	0.68737	−123.15 ± 1.21
597.70	15.19	0.26427	0.03441	0.70126	−107.27 ± 0.66
597.71	15.14	0.36934	0.04664	0.71335	−97.36 ± 0.61
597.69	15.19	0.49927	0.06137	0.72827	−88.33 ± 0.52
597.70	15.15	0.74990	0.08654	0.75328	−70.48 ± 0.52
597.72	15.19	0.9946	0.11074	0.77757	−60.44 ± 0.37
597.76	15.15	1.5007	0.15459	0.82119	−42.07 ± 0.30
597.70	15.13	2.0977	0.20386	0.87056	−29.62 ± 0.26

[a] The number of significant digits reported for m and V_ϕ (exp) exceeds the standard error by one to ensure fitted equations can be reproduced. [b] Calculated from $\Delta\rho = \rho - \rho_w^*$ with ρ_w^*, the density of water, obtained from Hill's equation of state.[16]

of either NaCl(aq) and/or D_2O to water. The densimeter was calibrated at the beginning, middle, and end of each day. For the Na_2HPO_4(aq) and Na_3PO_4(aq) solutions at all temperatures and for NaH_2PO_4(aq) at temperatures between 473 K and 523 K, the densimeter was calibrated with a standard solution of NaCl(aq). For NaH_2PO_4(aq) at 598 K, D_2O (mole fraction 0.998 D) was used as a reference. Both standards were used for NaH_2PO_4(aq) at 573 K. The densities of water, D_2O, and NaCl(aq) at every temperature and pressure were obtained from the equations of state reported by Hill,[16] Hill et al.,[17] and Archer,[18] respectively. The combined uncertainty in the measured relative densities, $(\rho - \rho_w^*)$, is estimated to be ± 0.0002 $g\cdot cm^{-3}$ arising from the sensitivity limits of the instrument itself (± 0.00004 $g\cdot cm^{-3}$), consistent with the standard error of the mean of the period of vibration (typically $7\cdot 10^{-9}$ s) and the accuracy of the reference data.

The relative density of each NaH_2PO_4(aq) solution was measured between 473.15 K ≤ T ≤ 598.15 K and each Na_2HPO_4(aq) solution was measured between 473.15 K ≤ T ≤ 573.15 K. Measurements on the Na_3PO_4(aq) solutions were made at four temperatures in the range 373.15 K ≤ T ≤ 498.15 K, two of which were repeated to ensure reproducibility. At the concentrations used in this work, aqueous solutions of Na_2HPO_4(aq) could not be studied above 573.15 K because a region of liquid−liquid immiscibility is known to exist.[19] The experimental temperatures used for Na_3PO_4(aq) were limited by the solubility of the salt, which decreases substantially at temperatures above 523 K.[20] Moreover, molalities used for the most dilute solutions of Na_3PO_4(aq) were restricted by the degree of hydrolysis, which causes $H_2PO_4^-$(aq) to become the dominant species at low concentrations.[4] The average pressure of all experiments was (15.06 ± 0.07) MPa.

Results

Apparent Molar Volumes. The experimental apparent molar volumes, V_ϕ (exp), were obtained from the equation

$$V_\phi(\mathrm{exp}) = \frac{-\Delta\rho}{m\rho\rho_w^*} + \frac{M}{\rho} \tag{2}$$

where $\Delta\rho = (\rho - \rho_w^*)$, is the density of the solution (ρ) relative to water (ρ_w^*), m is the stoichiometric molality, and M is the molar mass of the solute, NaH_2PO_4, Na_2HPO_4, or Na_3PO_4.[21] The experimental relative densities and apparent molar volumes are tabulated in Tables 1 to 3, along with their standard errors.

Because of the uncertainty in the speciation calculations, we have preferred to adopt two alternative approaches for describing the concentration dependence of the apparent molar volume results. The first treatment neglects the contribution of minor species, and it is based on the Pitzer-ion interaction model.[22] The results for the solutions of NaH_2PO_4 and Na_2HPO_4 are presented below. The second approach, which includes a treatment of speciation based on Young's rule,[23] is presented

Table 2. Experimental Relative Densities, $\Delta\rho = (\rho - \rho_w^*)$ and Apparent Molar Volumes, V_ϕ (exp) for Na_2HPO_4 (aq) from T = 473 K to 570 K and p = 15 MPa[a]

T / K	P / MPa	m / $mol \cdot kg^{-1}$	$\Delta\rho$ / $g \cdot cm^{-3}$	ρ^b / $g \cdot cm^{-3}$	V_ϕ (exp) / $cm^3 \cdot mol^{-1}$
T = (473.11 ± 0.02) K; p = (14.99 ± 0.01) MPa					
473.12	14.99	0.09825	0.00861	0.88791	−16.90 ±0.70
473.12	14.99	0.09920	0.02358	0.88809	−18.40 ± 0.81
473.10	14.99	0.20025	0.03223	0.90146	−12.71 ± 0.50
473.11	14.99	0.24952	0.04255	0.91904	−11.00 ± 0.48
473.09	14.99	0.29967	0.06339	0.91382	−8.07 ± 0.43
473.12	14.99	0.34155	0.08245	0.90784	−7.18 ±0.38
473.12	14.99	0.39991	0.12008	0.92615	−5.81 ± 0.39
473.08	14.99	0.49637	0.16133	0.93830	−5.08 ± 0.35
T = (522.85 ± 0.02) K; p = (15.19 ± 0.02) MPa					
522.86	15.17	0.09825	0.01474	0.82649	−50.97 ±1.36
522.86	15.16	0.09877	0.01468	0.82647	−50.66 ± 1.36
522.85	15.19	0.09920	0.01467	0.82642	−48.80 ± 1.29
522.84	15.18	0.20025	0.02845	0.84024	−39.58 ± 0.69
522.83	15.19	0.24952	0.04726	0.85907	−37.21 ± 0.70
522.84	15.21	0.29967	0.04159	0.85342	−33.77 ±0.65
522.84	15.20	0.34155	0.03521	0.84702	−32.90 ± 0.55
522.83	15.21	0.39991	0.05478	0.86661	−30.84 ± 0.52
522.89	15.20	0.49637	0.06669	0.87843	−26.96 ± 0.44
T = (548.19 ± 0.04) K; p = (15.03 ± 0.03) MPa					
548.19	15.01	0.09825	0.01599	0.78824	−85.88 ±0.85
548.18	15.00	0.09877	0.01612	0.78842	−85.74 ± 1.17
548.15	15.00	0.09920	0.01590	0.78813	−86.85 ± 0.83
548.15	15.01	0.20025	0.03048	0.80279	−68.95 ± 0.58
548.22	15.06	0.24952	0.04969	0.82194	−62.20 ± 0.49
548.16	15.03	0.29967	0.04402	0.81634	−58.84 ±0.53
548.19	15.02	0.34155	0.03713	0.80938	−56.18 ± 0.44
548.24	15.07	0.39991	0.05719	0.82943	−52.07 ± 0.42
548.24	15.06	0.49637	0.06932	0.84156	−46.36 ± 0.38
T = (570.50 ± 0.05) K; p = (15.05 ± 0.01) MPa					
570.56	15.04	0.09825	0.01713	0.74838	−127.91± 1.07
570.46	15.03	0.09877	0.01729	0.74846	−127.19 ± 1.39
570.50	15.04	0.09920	0.01706	0.74811	−128.88 ± 1.22
570.58	15.05	0.20025	0.03261	0.76364	−106.15 ± 0.76
570.47	15.06	0.24952	0.05269	0.78388	−97.90 ± 0.72
570.49	15.06	0.29967	0.04672	0.77796	−91.28 ± 0.64
570.50	15.04	0.34155	0.03975	0.77103	−87.70 ± 0.57
570.45	15.07	0.39991	0.06056	0.79188	−82.15 ±0.58
570.46	15.07	0.49637	0.07320	0.80451	−74.38 ± 0.52

[a] The number of significant digits reported for m and V_ϕ (exp) exceeds the standard error by one to ensure fitted equations can be reproduced. [b] Calculated from $\Delta\rho = \rho - \rho_w^*$ with ρ_w^*, the density of water, obtained from Hill's equation of state.[16]

in the Discussion. As we will show, the Pitzer treatment provides an adequate representation of the apparent molar volumes of NaH_2PO_4(aq) and Na_2HPO_4(aq).

Because the hydrolysis of PO_4^{3-}(aq) in dilute Na_3PO_4 solutions is so large, it was necessary to work with highly concentrated solutions over a limited range of molalities. As a result, it was not possible to model the concentration dependence of V_ϕ (exp) for Na_3PO_4.

Pitzer Ion-Interaction Model for NaH_2PO_4(aq) and Na_2HPO_4(aq). In this work, as a first approximation we represented V_ϕ (exp) for mono- and disodium phosphate, at constant temperature and pressure by the Pitzer ion-interaction model:[22]

$$V_\phi(\text{exp}) = V^\circ(i,\text{aq}) + \nu|z_+z_-|\frac{A_V}{2b}\ln(1 + bI^{1/2}) + 2\nu_+\nu_-RT \left(\frac{m}{m_O}\right)\left[B_V(i,\text{aq}) + \nu_+z_+\left(\frac{m}{m_O}\right)C_V(i,\text{aq})\right] \quad (3)$$

where T is the average temperature during each experiment; R = 8.31447 $J \cdot K^{-1} \cdot mol^{-1}$; b = 1.2 $kg^{1/2} \cdot mol^{-1/2}$; m_O = 1 $mol \cdot kg^{-1}$; m is the stoichiometric molality of NaH_2PO_4 or Na_2HPO_4 in the experimental solutions; ν_+ and ν_- are the stoichiometric coefficients of the cation and anion, respectively; $\nu = (\nu_+ + \nu_-)$; z_+ and z_- are the charges of the cation and anion, respectively; $I = 1/2\ \Sigma\ m_iz_i^2$ is the ionic strength of the solution where m_i and z_i are the molality and the charge of ion i, respectively; $V^\circ(i,\text{aq})$ is the standard partial molar volume of the electrolyte and the term A_V is the Debye−Hückel limiting law slope for apparent molar volumes, calculated from the equations of Archer and Wang[24] and the equation of state of Hill[16] for water. The higher order terms $B_V(i,\text{aq})$ and $C_V(i,\text{aq})$ are the second and third virial coefficients for the apparent molar volumes with $B_V(i,\text{aq})$ described by

$$B_V(i,\text{aq}) = \beta^{(0)V} + \frac{2\beta^{(1)V}}{\alpha^2 I}[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})] \quad (4)$$

and α = 2.0 $kg^{1/2} \cdot mol^{-1/2}$. In this case, we have preferred to set $\beta^{(1)V}$ to zero because its inclusion does not improve the fit quality.

Equation 3 was fitted to the apparent molar volumes of NaH_2PO_4 and Na_2HPO_4 solutions in Tables 1 and 2 by the method of least-squares. The resulting values of $V^\circ(i,\text{aq})$, $B_V(\text{i},\text{aq})$, and $C_V(i,\text{aq})$ together with their standard error are tabulated in Table 4 for each experimental temperature. The fitted and experimental values of V_ϕ (exp), as well as the difference between the two, are plotted as a function of

Table 3. Experimental Relative Densities, $\Delta\rho = (\rho - \rho_w^*)$, and Apparent Molar Volumes, V_ϕ (exp) for Na_3PO_4 (aq) from T = 373 K to 497 K and p = 15 MPa[a]

T K	P MPa	m $mol\cdot kg^{-1}$	$\Delta\rho$ $g\cdot cm^{-3}$	ρ^b $g\cdot cm^{-3}$	V_ϕ (exp) $cm^3\cdot mol^{-1}$
T = (373.14 ± 0.03) K; p = (15.00 ± 0.01) MPa					
373.11	14.98	0.39865	0.06478	1.03001	−4.30 ±0.45
373.16	14.98	0.39973	0.06559	1.03080	−5.88 ± 0.41
373.12	14.99	0.40012	0.06582	1.03104	−6.29 ± 0.46
373.18	15.00	0.61731	0.09578	1.06099	3.00 ± 0.57
373.13	15.01	0.61731	0.09859	1.06384	−1.44 ± 0.42
373.11	15.01	0.61731	0.09781	1.06303	−0.20 ± 0.45
T = (422.74 ± 0.08) K; p = (15.07 ± 0.12) MPa					
422.81	14.96	0.39865	0.06649	0.99184	−16.46 ± 0.66
422.71	15.20	0.39865	0.06627	0.99184	−15.83 ± 0.28
422.81	14.96	0.39973	0.06795	0.99330	−19.91 ± 0.63
422.67	15.16	0.39973	0.06772	0.99330	−19.23 ± 0.29
422.82	14.96	0.40012	0.06748	0.99282	−18.47 ± 0.63
422.66	15.20	0.40012	0.06721	0.99282	−17.66 ± 0.33
422.83	14.95	0.61731	0.09969	1.02501	−10.33 ± 0.56
422.62	15.19	0.61731	0.09937	1.02501	−9.73 ± 0.27
422.84	14.95	0.61731	0.10013	1.02545	−11.08 ± 0.50
422.67	15.16	0.61731	0.09987	1.02545	−10.59 ± 0.23
422.80	14.94	0.61731	0.10065	1.02600	−11.95 ± 0.53
422.66	15.20	0.61731	0.10039	1.02600	−11.45 ± 0.24
T = (472.67 ± 0.02) K; p = (15.11 ± 0.02) MPa					
472.67	15.08	0.39865	0.06762	0.94279	−31.70 ± 0.37
472.67	15.09	0.39973	0.06693	0.94211	−29.08 ± 0.44
472.69	15.13	0.40012	0.06824	0.94342	−32.79 ± 0.38
472.68	15.11	0.61731	0.10092	0.97610	−23.42 ± 0.31
472.67	15.11	0.61731	0.10076	0.97601	−23.10 ± 0.28
472.62	15.13	0.61731	0.10068	0.97584	−22.97 ± 0.33
T = (497.40 ± 0.02) K; p = (14.98 ± 0.06) MPa					
497.37	14.92	0.39865	0.06745	0.91319	−39.57 ± 0.63
497.39	15.02	0.39865	0.07001	0.91580	−47.75 ± 0.29
497.37	14.93	0.39973	0.07068	0.91642	−49.27 ± 0.56
497.43	15.02	0.39973	0.06979	0.91553	−46.44 ± 0.27
497.36	14.93	0.40012	0.06865	0.91440	−42.58 ± 0.56
497.41	15.03	0.40012	0.07029	0.91606	−47.79 ± 0.24
497.41	14.93	0.61731	0.10517	0.95086	−39.45 ± 0.37
497.41	15.05	0.61731	0.10355	0.94933	−36.23 ± 0.22
497.41	14.93	0.61731	0.10492	0.95061	−38.97 ± 0.39
497.41	15.06	0.61731	0.1037	0.94950	−36.53 ± 0.22
497.4	14.93	0.61731	0.1054	0.95110	−39.90 ± 0.41
497.38	15.06	0.61731	0.1037	0.94953	−36.51 ± 0.22

[a] The number of significant digits reported for m and V_ϕ (exp) exceeds the standard error by one to ensure fitted equations can be reproduced. [b] Calculated from $\Delta\rho = \rho - \rho_w^*$ with ρ_w^*, the density of water, obtained from Hill's equation of state.[16]

the molality in Figures 1 and 2. As shown, the difference between the observed and calculated apparent molar volumes are less than ± 2 $cm^3\cdot mol^{-1}$ for every experiment.

A suitable global fitting equation was obtained by expressing the standard partial molar volume $V°(i,aq)$ and the Pitzer interaction parameters, $B_V(i,aq)$ and $C_V(i,aq)$, in terms of temperature and pressure, according to the relationships

$$V°(i,\mathrm{aq}) = q_1 + q_2T + \frac{q_3R\kappa_{T,\mathrm{w}}^*}{T} \tag{5}$$

$$B_\mathrm{V}(i,\mathrm{aq}) = q_4 + q_5T \tag{6}$$

$$C_\mathrm{V}(i,\mathrm{aq}) = q_6 + q_7T \tag{7}$$

where q_1 to q_7 are adjustable fitting parameters. Our choice was based on previous studies that have shown the compressibility of water, $\kappa_{T,w}^* = -(1/V_w^*)(\partial V_w/\partial p)_T$, to be a good variable to describe the high temperature behavior of the standard partial molar volume for aqueous solutes.[18,25,26] Values of $\kappa_{T,\,w}^*$ were calculated using the equation of state of Hill.[16] The temperature dependence of the $B_V(i,aq)$ and $C_V(i,aq)$ parameters were described well by eqs 6 and 7 without including a compressibility term.

The entire array of experimental data in Tables 1 and 2 for the apparent molar volumes of NaH_2PO_4(aq) and Na_2HPO_4(aq) up to 573 K and 548 K, respectively, and standard partial molar volumes at 298.15 K from refs 10 to 12 were used to optimize the parameters in eqs 5 to 7. No corrections were made to convert the low temperature data at p = 0.1 MPa to p = 15 MPa. We believe the error introduced by omitting the pressure dependence correction to these room temperature data is less than the uncertainty of their measurements.[5]

The fitted parameters for NaH_2PO_4(aq) and Na_2HPO_4(aq) are listed in Table 5. Data at 598 K for NaH_2PO_4(aq) and at 570 K for Na_2HPO_4(aq) were omitted because ion-association and/or hydrolysis reactions may be important at these temperatures as shown in Figures 3 and 4 where the experimental apparent molar volumes, V_ϕ(exp), for NaH_2PO_4 and Na_2HPO_4 are compared with the results of the global fits. As shown, the agreement is very good in the case of NaH_2PO_4(aq) up to 573 K within ± 2 $cm^3\cdot mol^{-1}$ and for Na_2HPO_4(aq) up to 548 K within ± 4 $cm^3\cdot mol^{-1}$. At higher temperatures, the fitted equations do not accurately reproduce the experimental data, and for that reason

Table 4. Isothermal Fitting Parameters for the Pitzer Model for V_ϕ of NaH_2PO_4(aq) and Na_2HPO_4(aq): Standard Partial Molar Volumes, $V°$, Debye-Hückel Limiting Slopes, A_V, and Ion Interaction Parameters, B_V and C_V, according to equation 3[a]

T / K	p / MPa	$V°$ / $cm^3 \cdot mol^{-1}$	A_V[b] / $cm^3 \cdot kg^{1/2} \cdot mol^{-3/2}$	$B_V \cdot 10^3$ / MPa^{-1}	$C_V \cdot 10^4$ / MPa^{-1}
			NaH_2PO_4(aq)		
473.38	15.09	15.29 ± 0.56	13.3484	0.2799 ± 0.0645	
522.85	15.01	−11.56 ± 0.48	29.0884	1.0492 ± 0.1474	−2.615 ± 0.676
572.93	15.02	−85.60 ± 0.49	85.4927	1.7213 ± 0.1327	−5.678 ± 0.609
597.71	15.16	−183.53 ± 0.63	192.743	−0.3384 ± 0.0647	
			Na_2HPO_4(aq)		
473.11	14.99	−34.23 ± 0.73	13.3091		
522.85	15.19	−84.90 ± 0.55	29.0143	−0.8910 ± 0.1093	
548.19	15.03	−143.46 ± 0.56	47.4271	−1.0555 ± 0.1098	
570.50	15.05	−219.48 ± 0.92	80.0234	−5.1677 ± 0.4128	14.330 ± 3.674

[a] The number of significant digits reported for interaction parameters exceeds the standard error to ensure fitted equations can be reproduced. [b] Values of A_V were obtained from Archer and Wang's equation[24] and Hill's equation of state for water.[16]

Table 5. Global Fitting Parameters for the Pitzer Model for V_ϕ (exp) for NaH_2PO_4(aq) and Na_2HPO_4(aq)[a]

parameters for equation 5		parameters for equation 6		parameters for equation 7	
$V°$		B_V		C_V	
$cm^3 \cdot mol^{-1}$		MPa^{-1}		MPa^{-1}	
		NaH_2PO_4(aq)[b]			
q_1	95.191	$q_4 \cdot 10^3$	−6.5489	$q_6 \cdot 10^3$	2.6762
$q_2 \cdot 10^2$	−5.0700	$q_5 \cdot 10^5$	1.4464	$q_7 \cdot 10^6$	−5.6499
$q_3 \cdot 10^{-6}$	−3.94998				
		Na_2HPO_4(aq)[c]			
q_1	141.76	$q_4 \cdot 10^3$	1.52385		
$q_2 \cdot 10^1$	−1.1565	$q_5 \cdot 10^6$	−4.4294		
$q_3 \cdot 10^{-6}$	−8.32763				

[a] The number of significant digits reported for coefficients exceeds the standard error to ensure fitted equations can be reproduced. [b] Overall standard error of fit = 0.77 calculated from 29 points at four temperatures: 298.15 K (from refs 10 to 12), 473.38 K, 522.85 K, and 572.93 K and concentrations up to 2.1 molal. [c] Overall standard error of fit = 1.83 calculated from 28 points at four temperatures: 298.15 K, (from refs 10 to 12), 473.11 K, 522.85 K, and 548.19 K and concentrations up to 0.5 molal.

differences between the experimental and calculated values were omitted in the figures.

Discussion

Speciation Calculations. The analysis of apparent molar volumes is complicated by phosphate ionization equilibria

$$H_3PO_4(aq) + OH^-(aq) \leftrightarrows H_2PO_4^-(aq) + H_2O \qquad (8)$$

$$H_2PO_4^-(aq) + OH^-(aq) \leftrightarrows HPO_4^{2-}(aq) + H_2O \qquad (9)$$

$$HPO_4^{2-}(aq) + OH^-(aq) \leftrightarrows PO_4^{3-}(aq) + H_2O \qquad (10)$$

Mesmer and Baes[1] have reported equilibrium quotients, for the first and second dissociation reactions of H_3PO_4 in KCl at temperatures up to 573.15 K and ionic strengths up to 1.0 $mol \cdot kg^{-1}$. The speciation calculations for the effects of reactions 8 and 9 in our work are based on their model.

Values for the third ionization constant of H_3PO_4 have not been measured at temperatures above 423 K.[1] Equilibrium constants for reaction 10 were estimated using a simplified "density" model.[27,28] Details are given in the Appendix. Our calculated equilibrium constants for reaction 10 agree with those predicted by the revised Helgeson-Kirkham-Flowers (HKF) model used in the SUPCRT92 software[5–7] to within 0.02 at 473 K and 0.13 at 573 K in log K units. The agreement with these two, independent extrapolation methods suggests that the estimated values are reasonably accurate. Estimated activity coefficients from Lindsay's model[29,30] were used to describe the ion−ion interactions at finite molalities,

$$\gamma_{|z|} = (\gamma_{NaCl})^{z^2} \qquad (11)$$

with γ_{NaCl} calculated using the formulation by Archer.[18] Mesmer and Baes[1] have reported equilibrium quotients for the neutralization of HPO_4^{2-}(aq), reaction 10, in (0.5 and 1.0) $mol.kg^{-1}$ KCl, log $Q_{a,3}$ = 0.6 and 0.5 at 423 K, and log $Q_{a,3}$ = 1.14 and 1.23 at 373 K. These values compare reasonably well with those calculated by using our simplified "density" model and eq 11 at the same ionic strengths, log $Q_{a,3}$ = 0.37 and 0.47 at 423 K, and log $Q_{a,3}$ = 0.92 and 0.98 at 373 K, respectively.

Speciation calculations were carried out by solving the mass and charge balance equations with a modified version of the software EQBRM for Matlab.[31] The calculation made use of ionic-strength-dependent concentration quotients, Q_a and Q_w, calculated from the equilibrium constants and activity coefficient models for the ionization of phosphoric acid and water in refs 1 and 32, respectively. The value for the third ionization quotient $Q_{a,3}$ was obtained from equations in the Appendix. Because concentration quotients depend on ionic strength, an iterative procedure was used to recalculate the equilibrium concentration quotients until convergence was achieved. The results are shown in Figure 5.

The speciation calculations for the NaH_2PO_4 solutions show a very minor contribution of HPO_4^{2-}(aq) and H_3PO_4(aq) due to reactions 8 and 9 with the exception of the most concentrated solutions for which the total contribution of the two minor species reached up to ≈ 5 % at the highest temperature, 598.15 K. This temperature is outside the range at which equilibrium constants for these reactions were measured, and the speciation of the solution was determined by extrapolating the model proposed by Mesmer and Baes.[1]

Speciation results for the Na_2HPO_4(aq) solutions show that the contribution of $H_2PO_4^-$(aq) by hydrolysis of HPO_4^{2-}(aq) can reach up to almost 10 % in the most dilute solutions, while the contribution of PO_4^{3-}(aq) was relatively small (< 2 %) over the concentration and temperature ranges covered by this study.

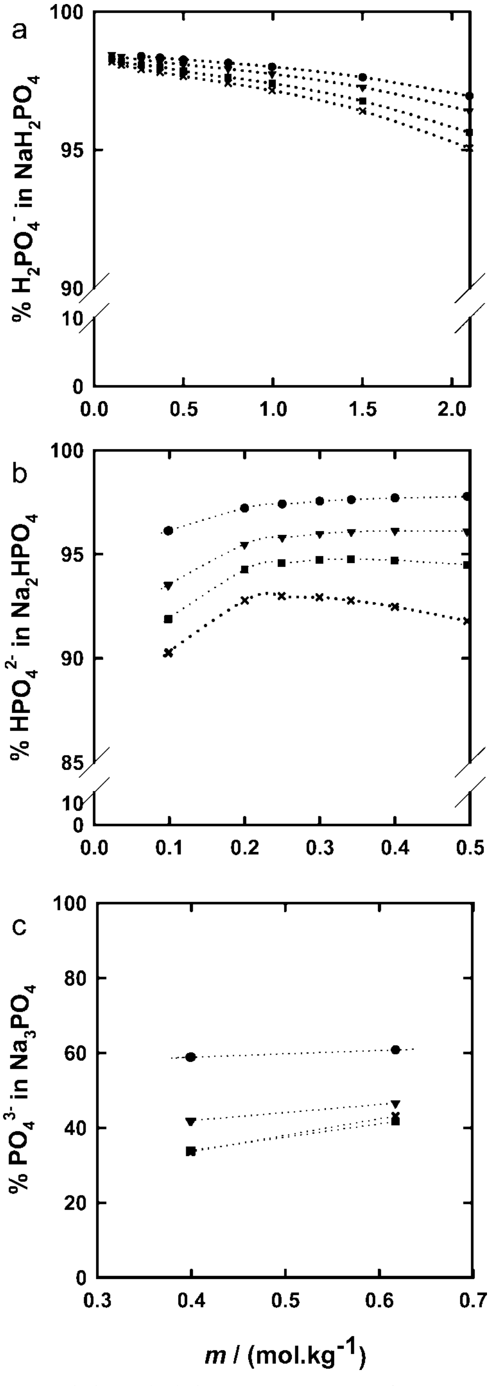

Figure 5. . Speciation calculations: (a) percentage of $H_2PO_4^-$(aq) in the NaH_2PO_4 solutions at •, 473 K; ▼, 523 K; ■, 573 K; ×, 598 K; (b) percentage of HPO_4^{2-}(aq) in the Na_2HPO_4 solutions at •, 473 K; ▼, 523 K; ■, 548 K; ×, 570 K; and (c) percentage of PO_4^{3-}(aq) in the Na_3PO_4 solutions at: •, 373 K; ▼, 423 K; ■,473 K; ×, 497 K. Lines for visualization purpose only.

The hydrolysis of PO_4^{3-}(aq) in the Na_3PO_4 solutions to form HPO_4^{2-}(aq) and OH^-(aq) was quite significant, ≈ 50 % at every temperature.

Young's Rule Model for NaH_2PO_4(aq) and Na_2HPO_4(aq). The previous model neglects the hydrolysis and the neutralization reactions, so a second attempt was made to determine the apparent molar volumes of the electrolyte species $V_\phi(i,\text{aq})$ from the experimental $V_\phi(\text{exp})$ values. In this approach, the contribution of the minor species was estimated from Young's rule,[23] which states that the measured experimental values, $V_\phi(\text{exp})$, are equal to the sum of the apparent molar volumes of all the solutes in solution, $V_\phi(i,\text{aq})$, at the ionic strength of the total solution in proportion to their fraction of the stoichiometric molality, $F_i = m_i/(m_1 + m_2 + \ldots.)$ plus an excess mixing term, $\delta(I)$

$$V_\phi(\text{exp}) = \sum_i F_i V_\phi(i,\text{aq}) + \delta(I) \tag{12}$$

As in previous work,[33,34] the excess mixing term, $\delta(I)$, was assumed to be negligible when compared with the other terms. With this approximation, the expression for monosodium phosphate is given by

$$V_\phi(\text{exp}) = (1 - \alpha_2 - \alpha_1)V_\phi(\text{NaH}_2\text{PO}_4,\text{aq}) + \alpha_2 V_\phi(\text{Na}_2\text{HPO}_4,\text{aq}) + \alpha_1 V_\phi(\text{H}_3\text{PO}_4,\text{aq}) + (\alpha_1 - \alpha_2)V_\phi(\text{NaOH},\text{aq}) + (\alpha_1 - \alpha_2)V_w^* \tag{13}$$

where $\alpha_1 = m(H_3PO_4)/m_T$ and $\alpha_2 = m(HPO_4^{2-})/m_T$ and m_T is the stoichiometric molality of phosphate in the solution

For the disodium phosphate salt, the expression is given by

$$V_\phi(\text{exp}) = (1 - \alpha_2 - \alpha_1)V_\phi(\text{Na}_2\text{HPO}_4,\text{aq}) + \alpha_2 V_\phi(\text{Na}_3\text{PO}_4,\text{aq}) + \alpha_1 V_\phi(\text{NaH}_2\text{PO}_4,\text{aq}) + (\alpha_1 - \alpha_2)V_\phi(\text{NaOH},\text{aq}) + (\alpha_1 - \alpha_2)V_w^* \tag{14}$$

with $\alpha_1 = m(H_2PO_4^-)/m_T$ and $\alpha_2 = m(PO_4^{3-})/m_T$.

As shown in Figure 5, the contribution of H_3PO_4 and Na_2HPO_4 is very small in the case of the NaH_2PO_4 solutions with no more than 5 % at the highest molality. We have estimated the correction in the apparent molar volumes for NaH_2PO_4(aq) based on the experimental values of $V_\phi(Na_2HPO_4,\text{aq})$ and the $V_\phi(H_3PO_4,\text{aq})$ values reported by Ballerat-Busserolles et al.[8] The correction was found to be negligible and within the experimental uncertainly at temperatures up to 573 K. As a result, the corrected values of $V_\phi(NaH_2PO_4,\text{aq})$ agree with the description given by the Pitzer model without speciation.

The contributions of other phosphate species in the Na_2HPO_4 solutions plotted in Figure 5 are larger, especially at low molalities where the contribution from reaction 9 can exceed 9 %. Corrected apparent molar volumes for Na_2HPO_4(aq) were calculated using the values of $V_\phi(NaH_2PO_4,\text{aq})$ obtained with eqs 5 to 7 and the coefficients in Table 5. Values for $V_\phi(\text{NaOH},\text{aq})$ were calculated at the same ionic strength as the Na_2HPO_4 solutions in Table 6 from equations reported by Corti and Simonson.[26] In this calculation, V_ϕ (Na_3PO_4,aq) was approximated by the first two terms in eq 3, namely $V°(Na_3PO_4,\text{aq})$ and the Debye−Hückel limiting law term. $V°(Na_3PO_4,\text{aq})$ values were calculated from the HKF model.[5–7] The values of $V_\phi(Na_2HPO_4,\text{aq})$, corrected for speciation, are summarized in Table 6 along with the experimental values. As shown, the difference between them is very small up to 548 K and concentrations up to ≈ 0.4 molal but becomes more important as temperature and concentration increase. While the agreement appears to be fortuitous, the correction is small and probably lies within the uncertainly in the calculations because these involve (i) extrapolated room temperature equilibrium constants for the third dissociation of phosphoric acid, (ii) estimated values of $V_\phi(Na_3PO_4,\text{aq})$ from SUPCRT92, and (iii) the assumption that no ion-pairing is present. Again, our conclusion is that the Pitzer model without speciation consideration provides an adequate representation of the experimental data.

Apparent Molar Volumes of Na_3PO_4(aq). Experiments were only carried out in a limited concentration range for the trisodium phosphate system because the degree of hydrolysis

Table 6. Experimental and Corrected Apparent Molar Volumes, V_ϕ(exp) and $V_\phi(i,\text{aq})$, for Na_2HPO_4(aq)

m / $\text{mol}\cdot\text{kg}^{-1}$	I^a / $\text{mol}\cdot\text{kg}^{-1}$	V_ϕ(exp) / $\text{cm}^3\cdot\text{mol}^{-1}$	$V_\phi(Na_2HPO_4,\text{aq})$ / $\text{cm}^3\cdot\text{mol}^{-1}$	I^a / $\text{mol}\cdot\text{kg}^{-1}$	V_ϕ(exp) / $\text{cm}^3\cdot\text{mol}^{-1}$	$V_\phi(Na_2HPO_4,\text{aq})$ / $\text{cm}^3\cdot\text{mol}^{-1}$
	$T = 473.11$ K; $p = 14.99$ MPa				$T = 522.85$ K; $p = 15.19$ MPa	
0.09825	0.2917	-16.9 ± 0.7	-17.0	0.2892	-51.0 ± 1.4	-50.9
0.09920	0.2945	-18.4 ± 0.8	-18.6	0.2920	-48.8 ± 1.3	-48.6
0.20025	0.5978	$-12.7 \pm 0\ 0.5$	-12.8	0.5952	-39.6 ± 0.7	-39.6
0.24952	0.7459	-11.0 ± 0.5	-11.1	0.7434	-37.2 ± 0.7	-37.4
0.29967	0.8968	-8.1 ± 0.4	-8.1	0.8946	-33.8 ± 0.7	-34.0
0.34155	1.0228	-7.2 ± 0.4	-7.2	1.0209	-32.9 ± 0.6	-33.2
0.39991	1.1984	-5.8 ± 0.4	-5.9	1.1970	-30.8 ± 0.5	-31.2
0.49637	1.4886	-5.1 ± 0.4	-5.2	1.4884	-27.0 ± 0.4	-27.5
	$T = 548.19$ K; $p = 15.03$ MPa				$T = 570.50$ K; $p = 15.05$ MPa	
0.09825	0.2877	-85.9 ± 0.9	-85.7	0.2864	-127.9 ± 1.1	-126.4
0.09877	0.2892	-85.7 ± 0.2	-85.6	0.2880	-127.2 ± 1.4	-125.7
0.09920	0.2905	$-86.9 \pm 0\ 0.8$	-86.8	0.2893	-128.9 ± 1.2	-127.6
0.20025	0.5939	-69.0 ± 0.6	-69.1	0.5935	-106.2 ± 0.8	-106.5
0.24952	0.7425	-62.2 ± 0.5	-62.5	0.7429	-97.9 ± 0.7	-99.0
0.29967	0.8941	-58.8 ± 0.5	-59.4	0.8956	-91.3 ± 0.6	-93.1
0.34155	1.0209	-56.2 ± 0.4	-57.0	1.0233	-87.7 ± 0.6	-90.2
0.39991	1.1979	-52.1 ± 0.4	-53.1	1.2017	-82.2 ± 0.6	-85.6
0.49637	1.4907	-46.4 ± 0.4	-49.4	1.4973	-74.4 ± 0.5	-79.3

[a] Speciation and ionic strength corresponding to reactions 8 to 10.

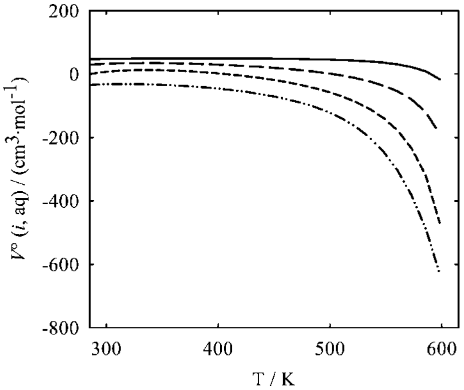

Figure 6. Comparison between standard molar volume of aqueous phosphate species, $V°(i,\text{aq})$, at $p = 15$ MPa: —, H_3PO_4(aq) from ref 8; — — NaH_2PO_4(aq) from this work; - - -, Na_2HPO_4(aq) from this work; -••-, Na_3PO_4(aq) from SUPCRT92.

to form HPO_4^{2-}(aq) + NaOH(aq) is large and difficult to quantify without accurate values for the third dissociation constant of phosphoric acid at high temperature.[1] In addition, the contribution of ion-pairs is expected to be very high under the conditions of these measurements because of the charge of the phosphate ion and temperature and concentrations involved. To our knowledge, the values of V_ϕ(exp) for Na_3PO_4(aq) in Table 3 are the first to be reported at elevated temperatures.

Standard Partial Molar Volumes. Values of $V°$ for the mono and disodium phosphate salts in Table 4 are plotted in Figure 6, where they are compared with data for H_3PO_4(aq) and Na_3PO_4(aq) taken from ref 8 and the HKF revised model (SUPCRT92 software),[5–7] respectively. As expected the standard molar volumes of the electrolytes are more negative than those for the neutral H_3PO_4(aq), while the qualitative difference between NaH_2PO_4(aq), Na_2HPO_4(aq), and Na_3PO_4(aq) is consistent with the difference in charge of the phosphate anions, $z = -1, -2$, and -3, respectively.

In Figure 7a,b, our values for $V°(NaH_2PO_4,\text{aq})$ and $V°(Na_2HPO_4,\text{aq})$ in Table 4 are compared to standard molar volumes predicted by SUPCRT92.[5–7] We have also included calculated values for $V°$ of NaH_2PO_4(aq) from the estimates of Ballerat-Busserolles et al.[8] for $V°(H_2PO_4^-,\text{aq})$ and $V°(Na^+,\text{aq})$ from SUPCRT92.[5–7]

As shown in Figure 7a, our values for $V°(NaH_2PO_4,\text{aq})$ are more negative than those predicted by SUPCRT92, which increasingly overestimates $V°$ (less negative values) with rising temperatures. On the other hand, the model proposed by Ballerat-Busserolles et al.[8] predicts partial molar volumes that are more negative than those found in this work, by more than 11 $\text{cm}^3\cdot\text{mol}^{-1}$ at 473 K and by 126 $\text{cm}^3\cdot\text{mol}^{-1}$ at 598 K. Figure 7b shows that SUPCRT92 also overestimates $V°(Na_2HPO_4,\text{aq})$ at high temperatures but to a lesser degree.

The discrepancy with SUPCRT92 undoubtedly arises because Shock and Helgeson's HKF parameters were derived only from low temperature volumetric data and the high-temperature ionization constants reported by Mesmer and Baes.[1] Ballerat-Busserolles et al.[8] derived the standard molar volumes from measurements of V_ϕ(exp) for solutions of aqueous H_3PO_4 in which $H_2PO_4^-$(aq) was a minor species. The uncertainties in their values are larger than those in this work.

Ion Association with Na^+(aq). The dihydrogen phosphate anion, $H_2PO_4^-$(aq), is isoelectronic with ClO_4^-(aq) and is not expected to undergo strong association with Na^+(aq). Holmes et al.[3] have reported unusually low activity coefficients for NaH_2PO_4(aq) at relatively low temperatures that according to the authors might be associated with sodium-phosphate ion-pairing and/or the formation of polymerized anions and ion pairs of the form $[(H_2PO_4)_nNa_{n-1}]^-$(aq) with $n \geq 2$.[35] In the absence of accurate formation constant data, the extent of association and/or polymerization reactions could not be quantified, however, our data up to 573 K are not consistent with formation of significant concentrations of polymerized anions or ion pairs. Ion pair formation is known to be favored at higher temperatures,[24,34,36] and may be the reason for the deviations from our simple Pitzer ion-association treatment observed at 598 K (Figure 3).

Na_2HPO_4(aq) is 2-1 electrolyte with a much stronger tendency to form ion-pairs. While, we expect a higher degree of association due to the charge of the anions and the temperature and concentration range covered by this study, ion-pairing between the phosphate anions and sodium has been neglected because no ion-association constants have been reported in the literature that could be used to account for their effect. Nevertheless, the results presented above do present strong evidence for the presence of ion pairs between Na^+ and HPO_4^{2-} as major species.

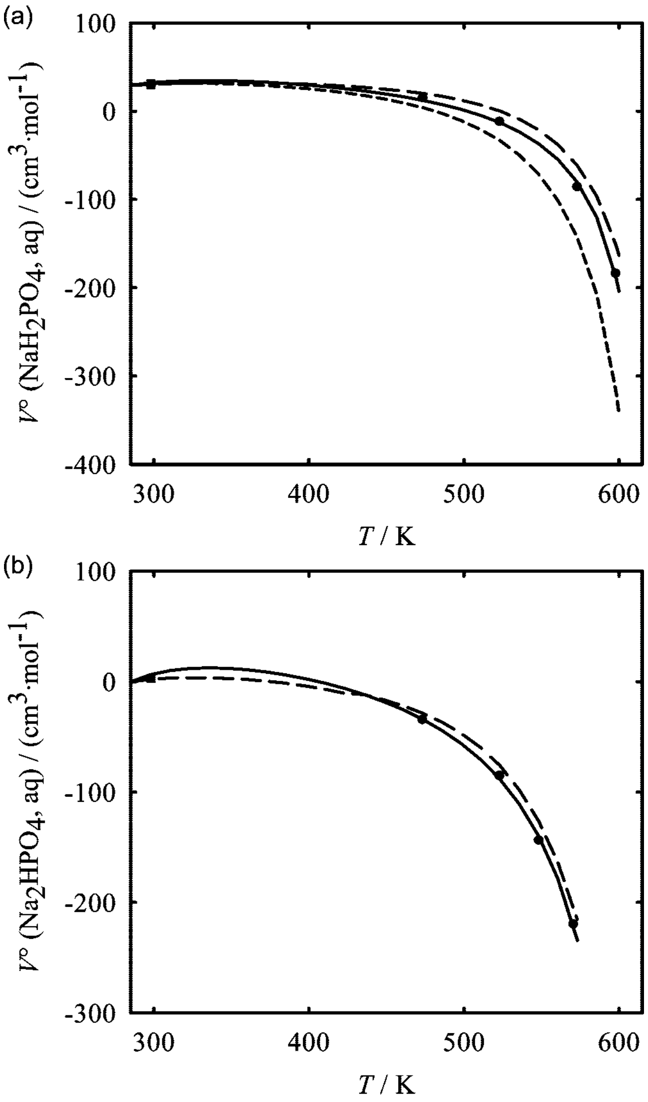

Figure 7. Standard molar volumes as a function of temperature at $p = 15$ MPa: (a) $V°(NaH_2PO_4,aq)$: ■, data at 298.15 K from refs 10 to 12; ●, isothermal fit values in Table 4; —, global fit of eqs 5 to 7 (Table 5); — —, SUPCRT92 model; - - -, $V°(NaH_2PO_4,aq) = V°(Na^+,aq)$ from SUPCRT92 + $V°(H_2PO_4^-,aq)$ from ref 8; (b) $V°(Na_2HPO_4,aq)$: ■, data at 298.15 K from refs 10 to 12; ●, this work isothermal fit and coefficients in Table 4; —, our global fit of eqs 5 to 7 (Table 5); — —, SUPCRT92 model.

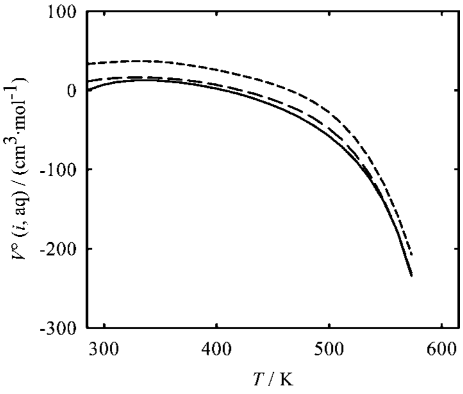

Figure 8. Standard molar volumes, $V°$(aq), of: —, Na_2HPO_4(aq) from this work; — —, Na_2SO_4(aq) from ref 36; - - -, K_2SO_4(aq) from ref 37; as a function of temperature at $p = 15$ MPa.

Activity coefficients for Na_2HPO_4(aq) recently reported by Holmes et al.[3] are lower than those for Na_2SO_4(aq), a salt that is known to form ion-pairs at high temperature, suggesting that even more ion association takes place in the disodium phosphate solutions. Our standard partial volume results for Na_2HPO_4(aq) are compared with those for Na_2SO_4(aq) and K_2SO_4(aq)[36,37] in Figure 8. At temperatures below 473 K, the three salts follow the anticipated trend for the charge/radius ratio of the cations and anions (Pauling-type crystal ionic radii: $Na^+ = 0.102$ nm;[38,39] $K^+ = 0.138$ nm;[38,39] $SO_4^{2-} = 0.230$ nm[38] and 0.215 nm;[39] and $HPO_4^{2-} = 0.230$ nm[39]), that is, $V°(K_2SO_4,aq) > V°(Na_2SO_4,aq) \approx V°(Na_2HPO_4,aq)$, while at temperatures higher than 500 K the three salts seem to converge toward very similar values. It is important to emphasize that this comparison was made with infinite dilution volumes of the nominal salts without any correction for ion-association. The converging behavior noted above suggests that an ion-pair, probably $NaHPO_4^-$(aq), becomes the dominant phosphate species in the Na_2HPO_4 solutions at the highest temperatures studied.

Conclusions

Apparent molar volumes for NaH_2PO_4(aq) and Na_2HPO_4(aq) at temperatures up to 598 and 570 K, respectively, have been reported for the first time. These data have been used to generate empirical equations that can be used to calculate standard partial molar volumes of both sodium phosphate salts at infinite dilution for all other temperatures within the conditions covered in this study.

The good agreement between the isothermal and global fits of $V_\phi(NaH_2PO_4,aq)$ up to 573 K suggest that ion pairing in monosodium phosphate solutions is small at low temperature and may increase notably at higher temperatures, as observed in the case of other 1:1 electrolytes.[25,26] There is a strong indication that ion-pairing might be important in the disodium phosphate solutions under hydrothermal conditions. This would be a fruitful area for further research which could, for example, be addressed using high-temperature AC conductance or Raman techniques.

A limited number of experimental values have been determined for the apparent molar volume of aqueous Na_3PO_4. Experimental values for ionization quotients and ion-pair formation constants are required to interpret the results more fully.

Appendix

Calculation of the Third Ionization Constant of Phosphoric Acid. Values for the third dissociation constant of phosphoric acid (reaction 10) were estimated using the simplified "density" model.[27,28] The equations take the form:

$$\ln K_{a,3}(\text{reaction 5}) = p_1 + \frac{p_2}{T} + \frac{p_3}{T} \cdot \ln(\rho_w^* / \rho_{w,Tr,pr}^*) \quad (A.1)$$

$$p_1 = \ln K_a(T_r) + \frac{\Delta_r H^o(T_r)}{RT_r} - \frac{\Delta_r C_p^o(T_r)\,\alpha_w^*(T_r, p_r)}{RT_r(\partial \alpha_w^* / \partial T)_{p_r}} \quad (A.2)$$

$$p_2 = -\frac{\Delta_r H^o(T_r)}{R} + \frac{(T_r \alpha_w^*(T_r, p_r) + \ln p_r)\Delta_r C_p^o(T_r)}{RT_r(\partial \alpha_w^* / \partial T)_{p_r}} \quad (A.3)$$

$$p_3 = -\frac{\Delta_r C_p^o(T_r)}{RT_r(\partial \alpha_w^* / \partial T)_{p_r}} \quad (A.4)$$

The "density" model relates the standard partial molar properties to the density of water ρ_w^*, the thermal expansivity $\alpha_w^* = -1/\rho_w^* (\partial \rho_w^* / \partial T)_P$, and its slope $(\partial \alpha_w^* / \partial T)_P$. Values for the adjustable parameters, $p_1 = -12.7421$, $p_2 = 4910.046$ K, and $p_3 = 527.978$ K were calculated from the recent NIST compilation for the PVT properties of water[40] and from the following values at 298.15 K and 0.1 MPa for the ionization of HPO_4^{2-}(aq) according to eq. 10, written as

$$\mathrm{HPO4^{2-}(aq) \leftrightarrows PO4^{3-}(aq) + H^{+}(aq)} \qquad (A.5)$$

$\ln K_3 = -12.375$,[41] $\Delta_r H° = 14653.8$ J.mol^{-1},[42] and $\Delta_r C_p° = -244$ J.K^{-1}.mol^{-1}.[12] Values for the ionization quotient of water were taken from Sweeton et al.[32]

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Received for review December 28, 2007. Accepted April 5, 2008. This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) and the University of Guelph.

JE700764H