412 *J. Chem. Eng. Data* **1995,** *40,* 412−414

Volumetric and Isopiestic Studies of ($H_2O + K_2HPO_4 + KH_2PO_4$) at 25 °C

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Density and water activity in ($H_2O + K_2HPO_4 + KH_2PO_4$) have been measured at 25 °C. The densities were measured by oscillating tube densimeter, and the water activities were obtained by an improved isopiestic technique. The results were correlated with semiempirical equations.

Introduction

Recently, there has been interest in utilizing aqueous salt−polymer two-phase systems for large scale biochemical purifications (*1, 2*). The salts employed in these systems must not be harmful to labile biomaterials. One of the salts commonly used is the mixture of potassium mono- and dihydrogen phosphates. Although there are reports on the thermodynamic properties of $H_2O + K_2HPO_4$ and $H_2O + KH_2PO_4$ binary systems (*3−5*), the ternary $H_2O + K_2HPO_4 + KH_2PO_4$ system has not been studied.

In this work, densities and water activities of this ternary system are measured at 25 °C. The correlations used to represent the experimental density and activity data depend on two parameters and single-electrolyte properties.

Experimental Section

Chemicals. The chemicals were all supplied by Merck (high purity) and were used without further purification. The salts were dried in oven at about 120 °C for 24 h, and the solutions were made from distilled and deionized water.

Apparatus and Procedure. The densimeter used in this study was a high-precision oscillating tube densimeter (DA-210, Kyoto Electronic Co., Japan). The accuracy of the instrument is reported to be ±0.01 $kg\cdot m^{-3}$, and it was calibrated with air and distilled water before each measurement. The temperature was held to within ±0.01 °C with a temperature controller (Eyela, UA-10, Tokyo Rikakikai Co., Japan).

The isopiestic apparatus employed is essentially similar to the one used previously (*6*). This apparatus consisted of a five-leg manifold attached to round-bottom flasks. The five flasks were typically used as follows. Two flasks contained the standard NaCl solutions, two flasks contained $K_2HPO_4 + KH_2PO_4$ solutions, and the central flask was used as a water reservoir. The apparatus was held in a constant temperature bath for at least 72 h for equilibration.

The temperature was controlled to within ±0.005 °C by a Heto temperature controller (Hetotherm PF, Heto Lab Equipment, Denmark). The temperature of the bath was monitored with a mercury thermometer with a readability of ±0.01 °C. After equilibrium had been reached, the manifold assembly was removed from the bath and each flask was weighed with a high-precision (±10^{-8} kg) analytical balance (AE-240, Mettler-Toledo AG, Switzerland).

Table 1. Densities of Aqueous K_2HPO_4 Solutions at 25 °C

$m/(mol\cdot kg^{-1})$	$d/(g\cdot cm^{-3})$	$m/(mol\cdot kg^{-1})$	$d/(g\cdot cm^{-3})$
0.1016	1.01180	0.6308	1.08414
0.1622	1.02051	1.4281	1.17987
0.1946	1.02504	2.4395	1.28582
0.2406	1.03161	3.7280	1.39826
0.2880	1.03801	5.7458	1.51245
0.3445	1.04565	8.6082	1.64466
0.3985	1.05303		

Table 2. Densities of Aqueous KH_2PO_4 Solutions at 25 °C

$m/(mol\cdot kg^{-1})$	$d/(g\cdot cm^{-3})$	$m/(mol\cdot kg^{-1})$	$d/(g\cdot cm^{-3})$
0.0502	1.00178	0.3941	1.03304
0.0991	1.00637	0.8128	1.06866
0.1464	1.01077	1.2805	1.10687
0.1988	1.01560	1.8370	1.14651
0.2968	1.02439		

Table 3. Densities of $H_2O + KH_2PO_4 + K_2HPO_4$ Solutions at 25 °C

$m/(mol\cdot kg^{-1})$		
KH_2PO_4	K_2HPO_4	$d_{12}/(g\cdot cm^{-3})$
0.2049	0.2976	1.05677
0.6149	0.8651	1.15840
0.4040	0.5658	1.10688
0.8082	1.1492	1.20248
1.0059	1.4345	1.24408
0.7231	0.7030	1.14759
1.1615	0.3485	1.13834
0.3213	0.3147	1.06856
0.4421	0.2516	1.07017
0.0796	0.1795	1.03028
0.4623	1.1211	1.17697
0.8640	0.2348	1.10140
0.1505	0.1214	1.02838
0.9296	0.7953	1.17219
1.4135	0.5121	1.17298

The maximum errors in the reported experimental molality, density, and activity data were verified as ±0.0002 $mol\cdot kg^{-1}$, ±0.00001 $g\cdot cm^{-3}$, and ±0.0002, respectively.

Results and Discussion

The results for the densities and water activities are given in Tables 1−6. The density data are correlated using the semiempirical equation

$$d_{12} - d_w = (d_1 - d_w) + (d_2 - d_w) + (m_1 m_2)^{1/2}(b_0 + b_1(m_1 m_2)^{1/2}) \quad (1)$$

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Table 4. Water Activity of H_2O + KH_2PO_4 Solutions at 25 °C

$m(KH_2PO_4)$/ $(mol{\cdot}kg^{-1})$	a	$m(KH_2PO_4)$/ $(mol{\cdot}kg^{-1})$	a
0.6874	0.9813	1.5709	0.9620
1.3325	0.9666	1.9158	0.9551
1.4546	0.9645	1.9913	0.9540

Table 5. Water Activity of H_2O + K_2HPO_4 Solutions at 25 °C

$m(K_2HPO_4)$/ $(mol{\cdot}kg^{-1}$	a	$m(K_2HPO_4)$/ $(mol{\cdot}kg^{-1})$	a
0.4371	0.9835	1.3034	0.9540
0.5353	0.9813	1.5673	0.9463
0.7644	0.9710	1.8157	0.9340
1.0124	0.9644	2.2007	0.9213
1.1609	0.9587		

Table 6. Water Activities a_{12} of H_2O + KH_2PO_4 + K_2HPO_4 Solutions at 25 °C

$m/(mol{\cdot}kg^{-1})$		
K_2HPO_4	KH_2PO_4	a_{12}
0.1572	0.1110	0.9906
0.2349	0.1655	0.9867
0.3025	0.2125	0.9831
0.2521	0.4518	0.9793
0.5867	0.1174	0.9758
0.4241	0.4430	0.9758
0.2281	0.7218	0.9758
0.5561	0.3909	0.9724
0.7999	0.4561	0.9634
0.2737	1.2433	0.9634
0.8861	0.4029	0.9619
0.3755	1.2166	0.9619

where d_{12}, d_1, d_2, and d_w represent the mass density of mixed-electrolyte "12" solution, single-electrolyte "1" solution, single-electrolyte "2" solution, and pure water, respectively. The coefficients b_0, and b_1 are empirical parameters, and m_1 and m_2 are the molalities of salts 1 and 2.

The densities of single-electrolyte solutions are obtained from

$$d_i = (1000 + m_iM_i)/[(1000/d_w) + m_i\phi_i] \qquad (2)$$

where M_i is the molecular weight and ϕ_i is the apparent molal volume of salt i. The apparent molal volume is given by the semiempirical equation

$$\phi_i = \phi_0 + S_v m_i^{1/2} + b_v m_i \qquad (3)$$

where ϕ_0 is the apparent molal volume at infinite dilution obtained from the experimental density data at very low salt concentration, b_v is a fitting parameter, and S_v is the theoretical limiting slope defined by

$$S_v = k[{}^1/_2\sum_i \nu_i z_i^2]^{3/2} \qquad (4)$$

where ν_i is the number of ions of species i and valency z_i formed by one molecule of electrolyte. The limiting slope, k, is 1.868 $cm^3{\cdot}L^{1/2}{\cdot}mol^{-3/2}$ at 25 °C (*7*). Equation 3 has been used to correlate the density data for a single-salt solution. The values for the infinite dilution apparent molar volume, ϕ_0, obtained from our density measurements were compared with the values estimated from the partial molar volumes of ions in water reported by Millero (*7*). The result of this comparison is given in Table 7 along with the values for b_v. The experimental density data for the H_2O + KH_2PO_4 system can be compared with sources compiled by Hellwege (*4*), who reported data with ±0.1 $kg{\cdot}m^{-3}$ accuracy at several different temperatures. As shown in Figure 1, our data compare well with those of ref 4.

Table 7. Apparent Molar Volume Parameter Values

	$\phi_0/(cm^3{\cdot}mol^{-1})$		
	a	b	$b_v/(cm^3{\cdot}kg{\cdot}mol^{-2})$
K_2HPO_4	24.70	25.74	1.14
KH_2PO_4	40.62	38.12	2.94

[a] This work. [b] Calculated from ionic partial molar volume data (*7*).

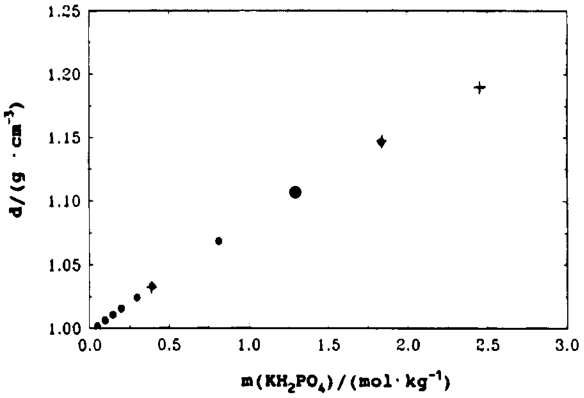

Figure 1. Comparison of the new experimental density results (●) for H_2O + KH_2PO_4 system with data (+) from sources compiled by Hellwege (*4*) at 25 °C.

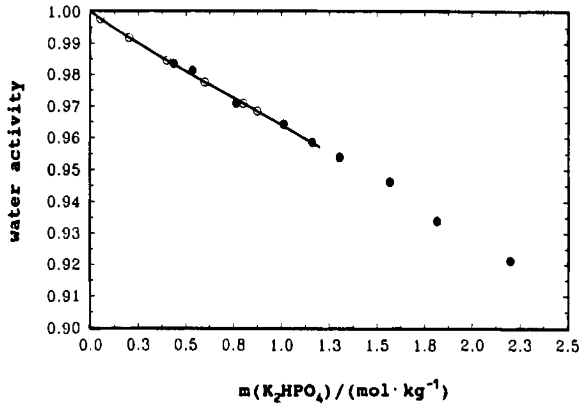

Figure 2. Comparison of the experimental water activity data (●) for H_2O + K_2HPO_4 system with literature values (○) of Goldberg (*5*) and Pitzer's correlation (—) at 25 °C.

For mixed electrolyte solutions, eqs 2 and 3 are used along with eq 1 to correlate the density results. The parameters b_0 and b_1 for this correlation are −0.000127 and −0.018857, and they can predict the density values with an average deviation of ±0.0005 $g{\cdot}cm^{-3}$.

The water activity results for single-salt solutions are given in Tables 4 and 5. As shown in Figure 2, our results for the H_2O + K_2HPO_4 system are in good agreement with the data given by Goldberg (*5*) and consistent with Pitzer's correlation at low concentrations. Likewise, for the H_2O + KH_2PO_4 system, our water activity data compare well with Pitzer's correlation. For both systems, our results extend the available activity data to higher molalities.

Furthermore, the water activity results for the mixed-salt solution are correlated by a similar equation

$$a_{12} - a_w = (a_1 - a_w) + (a_2 - a_w) + (m_1m_2)^{1/2}(b_0 + b_1(m_1m_2)^{1/2}) \qquad (5)$$

where a_{12}, a_1, a_2, and a_w represent the water activity of

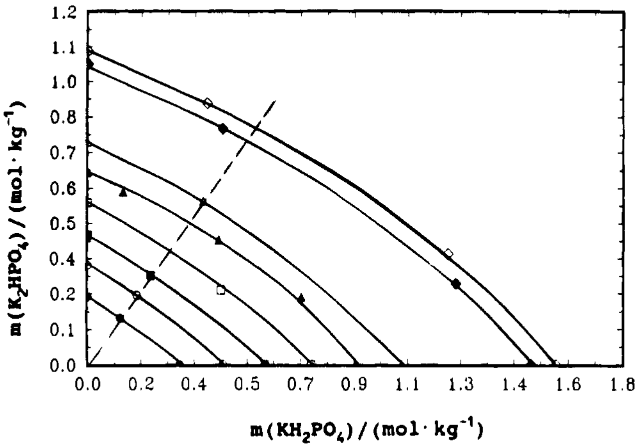

Figure 3. Water activity isolines for $H_2O + KH_2PO_4 + K_2HPO_4$ solutions at 25 °C corresponding to water activities 0.9906 (●), 0.9867 (○), 0.9831 (■), 0.9793 (□), 0.9758 (▲), 0.9724 (△), 0.9634 (◆), 0.9619 (◇).

mixed-salt 12 solution, single-salt 1 and 2 solutions, and pure water ($a_w = 1$). The single-salt water activities a_1 and a_2 are obtained from Pitzer osmotic coefficient correlations (*3*). The coefficients b_0 and b_1 are empirical parameters and for the $H_2O + K_2HPO_4 + KH_2PO_4$ system; they are equal to 0.00456 and 0.00927, respectively. These parameters predict the water activity with an average deviation of ±0.0002.

From the water activity results for the ternary solution, the lines of constant water activities are plotted in Figure 3. The molalities of each binary salt + H_2O solution for these lines (the points on the ordinate and abscissa) were calculated using Pitzer's correlation (*3*). Those activity values showing anomaly from smooth line were discarded. This method can be regarded as an additional check on the accuracy of the experimental water activities for the ternary system.

Moreover, some of the molality pairs given in Table 6 are selected such that the mass ratio of K_2HPO_4 to KH_2PO_4 is about 1.82. This ratio has been used in some of the experimental salt–polymer–water phase diagrams (*2*) because of its buffering action. The water activity results for these points are represented by a dashed line in Figure 3.

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Received for review June 29, 1994. Revised September 21, 1994. Accepted November 8, 1994.[⊗] This work is partially supported by the Sahand University of Technology, Research Grant 31-23. The density measurements were carried out at Tabriz University.

JE940123X

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1995.