PVT Properties of Concentrated Aqueous Electrolytes. 7. The Volumes of Mixing of the Reciprocal Salt Pairs KCl, K_2SO_4, NaCl, and Na_2SO_4 at 25 °C and I = 1.5 m

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The densities of mixtures of the six possible combinations of the salts KCl, NaCl, K_2SO_4, and Na_2SO_4 have been determined at constant ionic strength (I = 1.5 m) and 25 °C. The results have been used to determine the volume of mixing (ΔV_m) for these salts. The values of ΔV_m have been fit to equations of the form $\Delta V_m = y_2 y_3 I^2[v_0 + v_1(1 - 2y_3)]$ where y_i is the ionic strength fraction of salt i, and v_0 and v_1 are parameters related to the interaction of like charged ions. The cross-square rule was found to hold within the experimental error of the measurements.

Introduction

In recent papers (*1*, *2*) we have been interested in determining the excess volume and compressibility properties of the major components of natural waters. These results have been used to study the interactions of like charged ions and to estimate the *PVT* properties of natural brines (*3*).

In the present paper we will report on the volume of mixing the salts NaCl, KCl, Na_2SO_4, and K_2SO_4 which are the components of many natural waters.

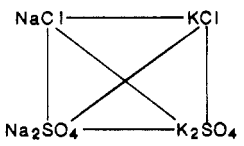
Experimental Section

The densities of NaCl, KCl, Na_2SO_4, and K_2SO_4 and their mixtures were measured at 25 °C by using a Picker vibrating flow densimeter (*4*). The instrument was calibrated with the known densities of water (*5*) and seawater (*6*). The temperature of the densimeter was controlled to ±0.001 °C with a Hallikainen thermotrol. The temperature was set and monitored with a Hewlett Packard quartz crystal thermometer calibrated with a platinum resistance thermometer and a G-2 Mueller bridge (IPTS-68).

All the solutions were made by weight with reagent-grade (Baker) chemicals and degassed ion-exchanged water (Millipore Super Q). The molalities of the stock solutions were checked from density measurements using the equations of state for these salt solutions (*7*, *8*).

Results and Calculations

The six possible mixtures of the salts studied can be represented by the cross-square diagram given below



The six possible mixtures are obtained by going around the sides and across both diagonals. The relative densities ($\rho - \rho_0$, g cm^{-3}) of these mixtures were measured at a constant ionic strength of 1.5 m and 25 °C. The results are given in Table I as a function of the ionic strength fraction ($y_3 = I_3/(I_2 + I_3)$, where subscripts 2 and 3 refer to different solutes and 1 is water).

Table I. Relative Densities ($\Delta\rho = \rho - \rho_0$, g cm^{-3}) of the Mixtures at 25 °C and I = 1.5 m

mixture	y_3	$10^3\Delta\rho$
NaCl (2)–KCl (3)	0	57.831
	0.1972	59.295
	0.3932	60.744
	0.4923	61.473
	0.6959	62.964
	0.7978	63.704
	1.0	65.169
KCl (2)–K_2SO_4 (3)	0	65.078
	0.1019	65.058
	0.2042	65.048
	0.3032	65.032
	0.4050	65.039
	0.5049	65.057
	0.6065	65.097
	0.7051	65.146
	0.8030	65.204
	0.9021	65.284
	1.0	65.372
K_2SO_4 (2)–Na_2SO_4 (3)	0	65.447
	0.1016	64.936
	0.2036	64.425
	0.3019	63.940
	0.4015	63.430
	0.5050	62.925
	0.6036	62.434
	0.7014	61.951
	0.8007	61.473
	0.9007	60.965
	1.0	60.472
NaCl (2)–Na_2SO_4 (3)	0	57.820
	0.1021	58.024
	0.2035	58.232
	0.4048	58.680
	0.5039	58.929
	0.6040	59.194
	0.7038	59.465
	0.8013	59.762
	0.9008	60.067
	1.0	60.399
NaCl (2)–K_2SO_4 (3)	0	57.428
	0.1010	58.171
	0.2015	58.916
	0.3024	59.677
	0.4028	60.459
	0.5030	61.256
	0.6029	62.064
	0.7019	62.888
	0.8015	63.728
	0.9010	64.594
	1.0	65.464
KCl (2)–Na_2SO_4 (3)	0	64.895
	0.1031	64.347
	0.2056	63.828
	0.3083	63.311
	0.4077	62.821
	0.5100	62.328
	0.6069	61.862
	0.7062	61.404
	0.8061	60.980
	0.9042	60.567
	1.0	60.204

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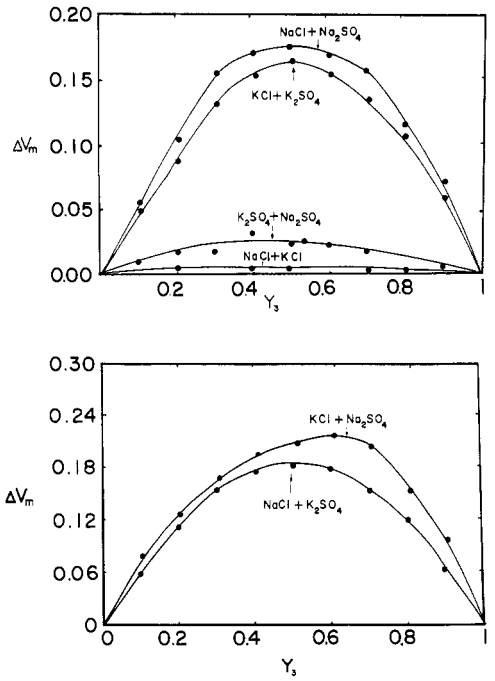

Figure 1. Values of the volume of mixing (ΔV_m) for the Na, K, Cl, SO_4 system at I = 1.5 m and 25 °C vs. the ionic strength fraction (y_3, where 3 is the second electrolyte).

For ternary mixtures of electrolyte (2) of molality m_2 and electrolyte (3) of molality m_3, the mean apparent molal volume, $\Phi_v(2,3)$, is given by

$$\Phi_v(2,3) = (M_T/\rho) - [10^3(\rho - \rho_0)/\rho_0 m_T] \quad (1)$$

where ρ and ρ_0 are, respectively, the densities of the solution and pure water, $M_T = (M_2m_2 + M_2m_3)/(m_2 + m_3)$ and the total molality $m_T = m_2 + m_3$ (M_i is the molecular weight of solute i). The apparent molal volumes $\phi_v(i)$ of the binary solutions were calculated from the measured densities

$$\phi_v(i) = (M_i/\rho) - [10^3 (\rho - \rho_0)/\rho_0 m_i] \quad (2)$$

The volumes of mixing, ΔV_m, for each mixture were determined from the experimental values of $\phi_v(i)$ and $\Phi_v(2,3)$ by using the equation

$$\Delta V_m = m_T\Phi_v(2,3) - m_2\,\phi_v(2) - m_3\phi_v(3) \quad (3)$$

The values of ΔV_m ($cm^3\ kg^{-1}\ H_2O$) for the various mixtures are shown in Figure 1 as functions of the ionic strength fractions, $y_3 = w_3m_3/(w_2m_2 + w_3m_3)$, where w_i are ionic strength factors (w = 1 for 1–1 electrolytes and 3 for 2–1 electrolytes). The values of ΔV_m for the side mixtures are related to the interactions of like charged ions. The largest values are found for the common cation mixtures for Cl–SO_4 interactions. The interactions between Na and K are quite small. These findings are in agreement with the heats of mixing for these mixtures (*9*).

The values of ΔV_m were fit to equation of the form (*10*)

$$\Delta V_m = y_2y_3I^2[v_0 + v_1(1 - 2y_3)] \quad (4)$$

where v_0 and v_1 are parameters related to ionic interactions (v_0 to cation–cation and anion–anion interactions and v_1 to triplet interactions, cation–anion–cation). The values of v_0 and v_1 for the various mixtures are given in Table II. With the exception of the KCl + Na_2SO_4 mixture the values v_1 are quite small and v_0 is directly related to the maximum value of ΔV_m ($=v_0 \times 0.25 \times 1.5^2$). The skew in the KCl + Na_2SO_4 system toward Na_2SO_4 may be related to changes in the ion pair $NaSO_4^-$ upon addition of KCl (see Figure 1).

Table II. Parameters v_0 and v_1 for the Eq $\Delta V_m = y_2y_3I^2[v_0 + v_1(1 - 2y_3)]$

mixtures	v_0[a]	v_1[a]	s[b]
NaCl (2)–KCl (3)	0.0070	0.0050	0.001 (1)
NaCl (2)–Na_2SO_4 (3)	0.3097	−0.0377	0.005 (6)
KCl (2)–K_2SO_4 (3)	0.2738	−0.0327	0.005 (6)
K_2SO_4 (2)–Na_2SO_4 (3)	0.0365	0.0206	0.005 (6)
NaCl (2)–K_2SO_4 (3)	0.3171	−0.0173	0.005 (6)
KCl (2)–Na_2SO_4 (3)	0.3979	−0.1056	0.007 (8)

[a] The units of v_0 and v_1 are cm^3 kg H_2O mol^{-2}. [b] The standard error in ΔV_m for eq 4, $cm^3\ kg^{-1}\ H_2O$. The errors in density (10^6 g cm^{-3}) are given in parentheses.

Table III. Verification of the Cross-Square Rule

common ion mixtures	ΔV_m(max)
NaCl–KCl	0.004 ± 0.001
Na_2SO_4–K_2SO_4	0.022 ± 0.005
NaCl–Na_2SO_4	0.175 ± 0.005
KCl–K_2SO_4	0.164 ± 0.005
	0.365 ± 0.02
uncommon ion mixtures	**ΔV_m(max)**
NaCl–K_2SO_4	0.182 ± 0.05
KCl–Na_2SO_4	0.217 ± 0.007
	0.399 ± 0.01
comparison of $\sum\square = X$	
$\sum\square$	0.365 ± 0.02
$\sum X$	0.399 ± 0.01
	0.034 ± 0.03

The volumes of mixing for the Na–K–Cl–SO_4 solutions can be used to examine the cross-square rule (*9*) which states that the sum of the volumes of mixing the common ion mixtures is equal to the cross mixtures

$$\sum\square = \sum X \quad (5)$$

where

$$\sum\square = \Delta V_m(\text{NaCl+KCl}) + \Delta V_m(\text{KCl+K}_2\text{SO}_4) + \Delta V_m(\text{K}_2\text{SO}_4\text{+Na}_2\text{SO}_4) + \Delta V_m(\text{Na}_2\text{SO}_4\text{+NaCl}) \quad (6)$$

and

$$\sum X = \Delta V_m(\text{NaCl+K}_2\text{SO}_4) + \Delta V_m(\text{KCl+Na}_2\text{SO}_4) \quad (7)$$

The verification of the cross-square rule for this mixture is shown in Table III. Within the experimental errors of the measurements the cross-square rule holds for the Na–K–Cl–SO_4 system at I = 1.5 m and 25 °C.

The *PVT* properties of the NaCl + K_2SO_4 and KCl + Na_2SO_4 solutions can be used to examine use of the equations of Wood and Reilly (*11*) to estimate the densities of solutions Na–K–Cl–SO_4. The mean apparent equivalent volume of a mixture is given by

$$\Phi_v = \sum_M\sum_X E_M E_X\,\phi_v(\text{MX}) + \Delta V_m/e_T \quad (8)$$

where E_i is the equivalent fraction of ion i, ϕ_v(MX) is the apparent equivalent volume of MX at the ionic strength of the mixture, ΔV_m is the volume of mixing the various components, and e_T is the total equivalents of the mixture. The volume of mixing term ($\Delta V_m/e_T$) has been formulated by Wood and Reilly (*11*) using the cross-square rule

$$\Delta V_m/e_T = (e_T/4)[\sum E_M E_N E_X v_0(\text{M,N})^X + \sum E_X E_Y E_M v_0(\text{X,Y})^M] \quad (9)$$

where $v_0(\text{M,N})^X$ and $v_0(\text{X,Y})^M$ are the volume of mixing interaction parameters for mixing, respectively, the cations M + N

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

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

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

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

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

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

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

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

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H_2O–H_3PO_4 media (1–14 mol/L) are characterized by means of the R_o(H) acidity function and the $R_o(H_2PO_4^-)$, $R_o(HPO_4^{2-})$, and $R_o(PO_4^{3-})$ functions which represent their ability to give up the proton and the $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} particles, respectively. Their solvation properties are characterized by means of the solvation-transfer activity coefficients of the solutes which are calculated from the normal potential values of the corresponding redox systems or from solubility product values. The significance of the parameter water activity is underlined.

Introduction

Phosphoric acid solutions produced in the industrial processing of phosphate ores are about 5.5 and 11.5 mol/L (30% and 50% P_2O_5). They contain valuable species such as uranium in the presence of iron, sulfate, and fluoride (hexafluorosilicate essentially) at fairly high concentrations (*1*) and others such as cadmium and arsenic which must be eliminated.

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

Results

1. R_o(H) Acidity Function. The R_o(H) acidity function (*2–4*) is determined from the variation with the acid concentration of the H^+/H_2 (hydrogen electrode) and the 1,4-benzoquinone/hydroquinone (Q/QH_2) redox system potentials ($E^a_{H^+/H2}$ and $E^a_{Qs/QH2s}$, respectively) referred to the ferrocenium/ferrocene (Fc^+/Fc) comparison system (Table I) according to the relations

$$R_o(H) = (E_o{}^w{}_{H^+/H2} - E^a{}_{H^+/H2})/0.058 \quad \text{with } E_o{}^w{}_{H^+/H2} = -0.400 \text{ V vs. } Fc^+/Fc \quad (1)$$

$$R_o(H) = (E^w{}_{Qs/QH2s} - E^a{}_{Qs/QH2s})/0.058 \quad \text{with } E^w{}_{Qs/QH2s} = +0.316 \text{ V vs. } Fc^+/Fc \quad (2)$$

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

2. $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} Anion Activities. By analogy with the R_o(H) acidity function, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-} anion activities are characterized by the $R_o(H_2PO_4^-)$, $R_o(HPO_4^{2-})$, and $R_o(PO_4^{3-})$ functions. $R_o(HPO_4^{2-}) = -\log a_{HPO_4^{2-}}$ and R_o-

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