Table IV. Mole Fraction at Which the Excess Volume Is Minimum[a]

	$x(V_m^E(\min))$	$V_m^E\min$	r_B/r_A
n-hexane	0.5900	−0.2995	0.8257
n-heptane	0.5684	−0.1506	0.8664
n-octane	0.5486	−0.0634	0.9036
n-nonane	0.5269	−0.0231	0.9380

[a] r_B/r_A is the ratio of molecular radius of B (*n*-undecane) and A (other *n*-alkane).

excess volume in minimum (see Table IV, which also lists approximate radii calculated from polarizabilities with use of molar refraction data (*12*)).

The absolute values of the excess volumes increased slightly with temperature. This effect too decreased as the length of the B chain increased. Temperature did not significantly affect the mole fraction at which the maximum absolute excess volume occurred. In interpreting these results, it must be borne in mind that at the working temperatures the molecules involved all have several significant conformations. Increasing temperature increases the proportion of higher energy conformations and so changes the feature of the intermolecular interactions. However, detailed explanation of our experimental results in these terms requires a conformational analysis that lies outside the scope of this article.

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Effect of Aluminum, Iron, and Magnesium upon the Solubility of α-Calcium Sulfate Hemihydrate in 40%, 45%, 50%, and 55% P_2O_5 Phosphoric Acid Solutions at 80, 90, 100, and 110 °C: Correlations with Water Concentration

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The influence of the common wet-process phosphoric acid impurities [Al_2O_3 (1.50%), Fe_2O_3 (2.15%), and MgO (0.50%)] upon the solubility of α-calcium sulfate hemihydrate in 40%, 45%, 50%, and 55% P_2O_5 phosphoric acid solutions at 80, 90, 100, and 110 °C, respectively, were measured. These additives were found to have very little influence upon α-$CaSO_4 \cdot 0.5H_2O$ solubility when the data are compared at equal water contents. The weight percent solubility in terms of anhydrous calcium sulfate is given by the equation $\% \; CaSO_4 = -0.39820685 + 0.00442936t + 0.00031947(\% \; H_2O)^2 + 0.00011517t(\% \; H_2O)$, where t is the temperature (°C) and % H_2O is the weight percent of water in the solution. Slight deviations in solubility are discussed in terms of enthalpy and entropy effects.

Introduction

Previously, we reported the solubility of α-calcium sulfate hemihydrate in phosphoric acid solutions ranging in concentrations from 40% to 55% P_2O_5 at temperatures of 80–110 °C (*1*). These are the concentration and temperature ranges of relevance for the production of concentrated wet-process phosphoric acid by "hemihydrate processes", i.e., processes in which phosphate rock is digested with sulfuric acid to produce phosphoric acid and insoluble byproduct calcium sulfate hemihydrate, $Ca(SO_4) \cdot 0.5H_2O$.

In the present publication, we describe the individual effects of typical concentrations of the phosphate rock derived impurities, Al, Fe, and Mg, upon the solubility of $CaSO_4 \cdot 0.5H_2O$ at P_2O_5 concentrations of 40–55% and temperatures of 80–110 °C. Limited work in this area has been conducted primarily by Russian investigators. For example, Kremenetskaya et al. (*2*) found that the combined effect of CaO and MgO was to lower the solubility of both $CaSO_4 \cdot 2H_2O$ and $CaSO_4 \cdot 0.5H_2O$ at P_2O_5 concentrations ranging from 30% to 40% and temperatures ranging from 60 to 90 °C. Shpunt et al. (*3*) obtained slight reductions in $CaSO_4 \cdot 0.5H_2O$ solubility with MgO alone at 80 °C and concentrations of 20–45% P_2O_5. Other investigators have studied the combined effect of Al_2O_3, F^-, and SiF_6^{2-} upon the solubilities and transition parameters for $CaSO_4 \cdot 2H_2O$–$CaSO_4 \cdot 0.5H_2O$–H_3PO_4 systems (*4*, *5*). In the cases investigated, the data were correlated in terms of P_2O_5 concentration rather than the total salt and acid content of the concentrated solutions.

In our previous publication (*1*), we also expressed the solubility data for the pure $CaSO_4 \cdot 0.5H_2O$–H_3PO_4–H_2O system in terms of weight percent P_2O_5 concentration and temperature. Since the concentration of water in an aqueous solution is inversely related to the concentrations of the remaining soluble components, it now appears of more general applicability to correlate the present and previous results in terms of water concentration and temperature, where "water concentration" (% H_2O) is defined as the calculated percentage of water present in the solutions, as determined by difference after as-

Table I. Weight Percent Solubility (as $CaSO_4$) of α-$CaSO_4 \cdot 0.5H_2O$ in 40%, 45%, 50%, and 55% P_2O_5 Phosphoric Acid Containing 1.5% Al_2O_3 at 80, 90, 100, and 110 °C

		wt %					
expt no.	temp, °C	P_2O_5	H_3PO_4	$AlPO_4$	$CaSO_4$	H_2O	K_{sp}
40-80-Al	80	40.24	52.71	3.55	0.939 ± 0.038	42.80	0.183
45-80-Al		45.14	59.47	3.56	0.680 ± 0.029	36.29	0.0961
50-80-Al		50.03	66.22	3.57	0.491 ± 0.022	29.72	0.0501
55-80-Al		54.91	72.95	3.58	0.349 ± 0.014	23.13	0.0253
40-90-Al	90	40.21	52.67	3.55	1.027 ± 0.022	42.75	0.219
45-90-Al		45.09	59.40	3.56	0.795 ± 0.023	36.24	0.131
50-90-Al		49.98	66.15	3.57	0.583 ± 0.019	29.70	0.0706
55-90-Al		54.87	72.90	3.57	0.423 ± 0.012	23.11	0.0372
40-100-Al	100	40.16	52.60	3.55	1.130 ± 0.029	42.72	0.265
45-100-Al		45.04	59.34	3.56	0.900 ± 0.026	36.21	0.168
50-100-Al		49.94	66.10	3.56	0.650 ± 0.021	29.69	0.0878
55-100-Al		54.85	72.87	3.57	0.444 ± 0.014	23.11	0.0410
40-110-Al	110	40.12	52.55	3.54	1.215 ± 0.019	42.69	0.307
45-110-Al		45.00	59.28	3.55	0.974 ± 0.011	36.19	0.197
50-110-Al		49.90	66.04	3.56	0.736 ± 0.013	29.66	0.113
55-110-Al		54.80	72.80	3.57	0.540 ± 0.010	23.09	0.0606

signing all cations and anions to their respective anhydrous salt and acid forms. This procedure offers the advantage of relating the solubilities to the total salt and acid contents of the concentrated solutions rather than simply to the phosphate concentration.

Experimental Section

The reagents and procedures employed in this investigation were described previously (*1*). Solutions containing 1.50% Al_2O_3 were prepared by dissolving 10.421 g $AlPO_4$ (Fisher Laboratory Chemical, purified, Lot No. 781866) in 280.0 g of 40.00%, 45.00%, 50.00%, and 55.00% P_2O_5 phosphoric acid solutions, respectively. Solutions containing 2.15% Fe_2O_3 were prepared by dissolving 3.161 g of Fe powder (Baker Analyzed Reagent, Lot No. 44613, 98.6%) in 200.0 g of the respective P_2O_5 stock solutions. The iron then was converted to the ferric state by addition of 4.61 g of 50% H_2O_2. Finally, solutions containing 0.50% MgO were prepared by dissolving 1.005 g of MgO (B&A, Lot. No. C3518173) in 200.0 g of the respective stock solutions.

The solubility studies were conducted as follows. A 1-g amount of α-$CaSO_4 \cdot 0.5H_2O$ (*1*) was added to each of 12 50-mL volumetric flasks. Aliquots of 20 mL each of the respective Al_2O_3-, Fe_2O_3-, and MgO-doped phosphoric acid solutions were added to each flask. The flasks were placed in a paraffin oil bath and heated at the desired temperature with stirring for a period of 1 h. The crystals of $CaSO_4 \cdot 0.5H_2O$ were then allowed to settle to the bottom, and the heating was continued for an additional 2 h at 80 and 90 °C or 1 h at 100 and 110 °C. The results of previous experiments (*1*) suggested that these heating times were of sufficient duration to allow the establishment of equilibrium. The supernatant liquid was sampled and subjected to sulfate analysis (triplicate determinations) using a Dionex Model 2210 ion chromatograph, as described previously (*1*). All solution concentrations were corrected to account for the dissolved $CaSO_4 \cdot 0.5H_2O$. The crystals were filtered out, washed with acetone, and dried. Microscopic and X-ray examination showed that the crystals were still in the form of calcium sulfate hemihydrate.

Results and Discussion

Our previously obtained data (Table I, ref 1) for the pure α-$CaSO_4 \cdot 0.5H_2O$–P_2O_5–H_2O system was correlated with the water concentration by converting the weight percent P_2O_5 concentrations to weight percent H_3PO_4. The free water content was calculated from the expression % H_2O = 100 − % H_3PO_4 − % $CaSO_4$. Multiple regression techniques were then used to express the solubilities (as % $CaSO_4$) in terms of water content (% H_2O) and temperature (t, °C). The best fit of the data (correlation coefficient, $R^2 = 0.997\,78$) was given by eq 1. [The data in terms of P_2O_5 concentration are given by % $CaSO_4 = 2.87918103 + 0.01399258t - 0.08942939(\%\ P_2O_5) + 0.00059658(\%\ P_2O_5)^2 - 0.00011850t(\%\ P_2O_5)$.]

$$(\%\ CaSO_4)_P = -0.44803198 + 0.00535374t + 0.00035094(\%\ H_2O)^2 + 0.0000982t(\%\ H_2O) \quad (1)$$

Table I gives the solubility of α-$CaSO_4 \cdot 0.5H_2O$ in systems containing approximately 40–55% P_2O_5 and 1.5% Al_2O_3. The data were best fit ($R^2 = 0.997\,04$) by eq 2. [The corresponding expression in terms of P_2O_5 concentration is % $CaSO_4 = 2.57119096 + 0.01893041t - 0.08804059(\%\ P_2O_5) - 0.00069412(\%\ P_2O_5)^2 - 0.00022856t(\%\ P_2O_5)$.]

$$(\%\ CaSO_4)_{Al} = 0.07019843 - 0.01702199(\%\ H_2O) + 0.00039262(\%\ H_2O)^2 + 0.00025107t(\%\ H_2O) \quad (2)$$

Table I also gives the apparent solubility product constants for α-$CaSO_4 \cdot 0.5H_2O$ in the Al_2O_3–H_3PO_4 systems as defined by the equation

$$K_{sp} = (\%\ Ca^{2+})(\%\ SO_4^{2-}) = 0.20773(\%\ CaSO_4)^2 \quad (3)$$

These are concentration values and are not corrected for ion activities, ion pair formation, etc. The apparent solubility product constants for the entire concentration and temperature field may be obtained by substituting eq 2 into eq 3.

Table II gives the solubility of α-$CaSO_4 \cdot 0.5H_2O$ in concentrated phosphoric acid systems containing 2.15% Fe_2O_3. The solubilities are given by eq 4 ($R^2 = 0.999\,37$). [The same data

$$(\%\ CaSO_4)_{Fe} = -0.32755470 + 0.00305471t + 0.00026300(\%\ H_2O)^2 + 0.00014505t(\%\ H_2O) \quad (4)$$

in terms of P_2O_5 concentration and temperature are given by % $CaSO_4 = 2.16646840 + 0.01665611t - 0.06977156(\%\ P_2O_5) + 0.00049508(\%\ P_2O_5)^2 - 0.00019300t(\%\ P_2O_5)$.]

Finally, Table III gives the solubility of α-$CaSO_4 \cdot 0.5H_2O$ in concentrated H_2PO_4 solutions containing 0.50% MgO. The solubility data are given by eq 5 ($R^2 = 0.999\,02$). [The same

$$(\%\ CaSO_4)_{Mg} = -0.18814228 + 0.00002070t^2 + 0.00028039(\%H_2O)^2 + 0.00013319t(\%\ H_2O) \quad (5)$$

data in terms of P_2O_5 concentration and temperature are given by % $CaSO_4 = 2.83423760 + 0.00745268t + 0.0000562t^2 - 0.07800622(\%\ P_2O_5) + 0.00059272(\%\ P_2O_5)^2 - 0.00021180t(\%\ P_2O_5)$.]

Examination of the solubilities predicted by eqs 1, 2, 4, and 5 suggests that the addition of Al_2O_3 (1.50%), Fe_2O_3 (2.15%), and MgO (0.50%) have very little effect upon the solubility α-$CaSO_4 \cdot 0.5H_2O$ for solutions containing equal water concen-

Table II. Weight Percent Solubility (as $CaSO_4$) of α-$CaSO_4\bullet0.5H_2O$ in 40%, 45%, 50%, and 55% P_2O_5 Phosphoric Acid Containing 2.15% Fe_2O_3 at 80, 90, 100, and 110 °C

		wt %					
expt no.	temp, °C	P_2O_5	H_3PO_4	$FePO_4$	$CaSO_4$	H_2O	K_{sp}
40-80-Fe1	80	38.27	50.19	4.08	0.953 ± 0.021	44.77	0.189
45-80-Fe2		43.14	56.92	4.09	0.751 ± 0.013	38.24	0.117
50-80-Fe3		48.04	63.67	4.10	0.542 ± 0.009	31.69	0.0610
55-80-Fe4		52.93	70.42	4.11	0.379 ± 0.007	25.09	0.0298
40-90-Fe1	90	38.23	50.14	4.08	1.069 ± 0.018	44.72	0.237
45-90-Fe2		43.11	56.87	4.09	0.833 ± 0.011	38.21	0.144
50-90-Fe3		48.00	63.62	4.10	0.614 ± 0.017	31.66	0.0783
55-90-Fe4		52.89	70.37	4.10	0.445 ± 0.008	25.07	0.0411
40-100-Fe1	100	38.20	50.10	4.08	1.148 ± 0.037	44.68	0.274
45-100-Fe2		43.07	56.82	4.08	0.923 ± 0.026	38.17	0.177
50-100-Fe3		47.96	63.57	4.09	0.695 ± 0.014	31.64	0.100
55-100-Fe4		52.86	70.33	4.10	0.505 ± 0.011	25.06	0.0530
40-110-Fe1	110	38.16	50.05	4.07	1.243 ± 0.014	44.64	0.321
45-110-Fe2		43.04	56.77	4.08	0.999 ± 0.022	38.14	0.207
50-110-Fe3		47.93	63.52	4.09	0.774 ± 0.012	31.61	0.124
55-110-Fe4		52.82	70.28	4.10	0.575 ± 0.009	25.05	0.0687

Table III. Weight Percent Solubility (as $CaSO_4$) of α-$CaSO_4\bullet0.5H_2O$ in 40%, 45%, and 55% P_2O_5 Phosphoric Acid Containing 0.5% MgO at 80, 90, 100, and 110 °C

		wt %					
expt no.	temp, °C	P_2O_5	H_3PO_4	$Mg_3(PO_4)_2$	$CaSO_4$	H_2O	K_{sp}
40-80-Mg1	80	39.38	53.58	1.08	0.978 ± 0.025	44.36	0.199
45-80-Mg2		44.42	60.53	1.08	0.739 ± 0.018	37.65	0.113
50-80-Mg3		49.46	67.49	1.08	0.541 ± 0.014	30.89	0.0608
55-80-Mg4		54.50	74.45	1.08	0.380 ± 0.012	24.09	0.0300
40-90-Mg1	90	39.35	53.54	1.08	1.048 ± 0.014	44.34	0.228
45-90-Mg2		44.38	60.48	1.08	0.824 ± 0.012	37.62	0.141
50-90-Mg3		49.43	67.45	1.08	0.601 ± 0.009	30.87	0.0750
55-90-Mg4		54.47	74.41	1.08	0.432 ± 0.005	24.08	0.0388
40-100-Mg1	100	39.31	53.48	1.07	1.162 ± 0.017	44.28	0.280
45-100-Mg2		44.33	60.41	1.08	0.919 ± 0.019	37.59	0.175
50-100-Mg3		49.38	67.39	1.08	0.687 ± 0.012	30.85	0.0980
55-100-Mg4		54.42	74.34	1.08	0.505 ± 0.006	24.07	0.0530
40-110-Mg1	110	39.26	53.41	1.07	1.266 ± 0.018	44.25	0.333
45-110-Mg2		44.28	60.34	1.08	1.014 ± 0.017	37.57	0.214
50-110-Mg3		49.33	67.31	1.08	0.781 ± 0.008	30.83	0.127
55-110-Mg4		54.38	74.29	1.08	0.573 ± 0.016	24.06	0.0682

Table IV. van't Hoff Parameters Associated with the Dissolution of α-$CaSO_4\bullet0.5H_2O$ in Concentrated H_3PO_4 (40–55% P_2O_5) as a Function of Water Concentration

% H_2O	pure system	1.5% Al_2O_3	2.15% Fe_2O_3	0.50% MgO	combined
		ΔH, cal/mol			
25	4167	3516	3870	4014	4032
30	3444	3260	3288	3398	3362
35	2921	3020	2876	2955	2881
40	2525	2804	2567	2619	2519
45	2219	2611	2324	2355	2237
			C		
25	5.018	4.079	4.531	4.770	4.801
30	4.281	3.986	4.000	4.182	4.141
35	3.786	3.889	3.663	3.796	3.707
40	3.446	3.800	3.439	3.532	3.412
45	3.207	3.725	3.285	3.347	3.207

trations at the same temperature. In most cases, the solubilities predicted for solutions containing Al, Fe, or Mg agree with those for the pure $CaSO_4\cdot0.5H_2O-H_3PO_4$ system to within the limits of the experimental error for sulfate analysis. There does, however, appear to be a slight reduction in solubility resulting from the addition of Al_2O_3 and Fe_2O_3.

In order to examine these effects further, the results predicted by eqs 1, 2, 4, and 5 at water concentrations of 25%, 30%, 35%, 40%, and 45% were regressed (correlation coefficients ranged from 0.998 to 0.999) in terms of the van't Hoff equation

$$\ln(\%\ CaSO_4) = (-\Delta H/RT) + C \qquad (6)$$

where ΔH is the apparent heat of solution at saturation, T is the absolute temperature (K), R is the universal gas constant (1.9872 cal/(deg·mol), and C is an integration constant that is related to the entropy of solution at saturation ($C = \Delta S/R$). Table IV gives the influence of Al, Fe, and Mg upon the apparent heats and entropies of solution.

As observed previously (*1*), the heat of solution of $CaSO_4\cdot0.5H_2O$ in the pure phosphoric acid systems becomes progressively more endothermic as the water content of the solutions is decreased (P_2O_5 content increased). Similar results are observed for the Al, Fe, and Mg systems. However, the addition of aluminum appears to give a significantly reduced spread of ΔH values. Similarly, the entropy-dependent integration factor, C, for the Al system shows much less variation with water concentration. Entropy is generally recognized as a measure of the randomness of a system. The increasing C values with decreasing water contents suggest decreased structuring of water molecules in the vicinity of ionic species as the solution concentration is increased. In the case of Al, this effect is apparently moderated, suggesting that the entropy effect is governed by a different mechanism—possibly the formation of a strong aluminum phosphate complex.

In any event, as indicated previously, the influence of each of the additives is small and it thus appears of practical utility to combine all of the data (Tables I–III and Table I of ref 1) into a single overall correlation with respect to temperature and water concentration. The results for the regression of the combined data are given by eq 7 ($R^2 = 0.991\,07$).

$$\%\ CaSO_4 = -0.39820685 + 0.00442936t + 0.00031947(\%\ H_2O)^2 + 0.00011517t(\%\ H_2O) \qquad (7)$$

The corresponding van't Hoff parameters are given in the last column of Table IV. [The solubility data in terms of temperature and % P_2O_5 concentration are given by % $CaSO_4$ = $2.58353564 + 0.01479136t - 0.08054436(\% P_2O_5) + 0.00054433(\% P_2O_5)^2 - 0.00014460t(\% P_2O_5)$.]

Finally, it should be noted that eqs 1, 2, 4, 5, and 7 give good estimates of the solubility of $CaSO_4 \cdot 0.5H_2O$ only when employed within the range of the experimental variables (Tables I-III and Table I of ref 1). They cannot be employed for extrapolations outside these ranges. Moderate extrapolations of the data may be made by using the van't Hoff equation.

Glossary

t	temperature, °C
R^2	correlation coefficient
ΔH	apparent heat of solution at saturation, cal/mol
C	integration constant
T	absolute temperature, K
R	gas constant, 1.9872 cal/(deg·mol)
K_{sp}	apparent solubility product constant, (% Ca)(% SO_4)
ΔS	apparent entropy of solution at saturation, cal/(deg·mol)

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High-Pressure Binary Vapor–Liquid Equilibrium Measurements of Carbon Dioxide with Aromatic Hydrocarbons

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High-pressure binary vapor–liquid equilibria of carbon dioxide with anisole and methylanisole isomers were determined at 333, 363, and 393 K and pressures up to 20 MPa. A circulation-type apparatus was built and tested by comparing the measured vapor–liquid equilibrium data of the carbon dioxide–toluene system at 393 K with literature values. In addition to temperature, pressure, and phase compositions, the vapor- and liquid-phase densities were measured for the binary systems of carbon dioxide with anisole and methylanisole isomers.

Introduction

The design and operation of separation processes requires knowledge of vapor–liquid equilibrium data. In particular, high-pressure phase equilibrium data for systems containing aromatic hydrocarbons will be needed to design and operate coal processing plants.

In this study, we have measured binary-phase equilibria of systems containing aromatic hydrocarbons (anisole and methylanisole isomers) as one of the components and carbon dioxide as the other component.

A circulation-type apparatus was built to measure temperature, pressure, vapor- and liquid-phase compositions, and vapor- and liquid-phase densities and was tested by comparing the vapor–liquid equilibrium data for the carbon dioxide–toluene system at 393 K with those of Ng and Robinson (*1*). This comparison showed good agreement. After testing the experimental apparatus, vapor–liquid equilibrium data for carbon dioxide–anisole, carbon dioxide–2-methylanisole, carbon dioxide–3-methylanisole, and carbon dioxide–4-methylanisole were measured at 333, 363, and 393 K and pressures ranging up to the mixture critical pressures.

Kim et al. (*2*) reported solubility data for carbon dioxide–anisole at 343.2 and 372.3 K and pressure ranging up to 16.8 MPa. However, no data are reported in the literature for carbon dioxide–2-methylanisole, carbon dioxide–3-methylanisole, and carbon dioxide–4-methylanisole systems.

Experimental Section

Apparatus and Procedure. Vapor- and liquid-phase densities, as well as vapor and liquid equilibrium compositions, can be measured at various temperatures, ranging from ambient temperature to 420 K, and various pressures, ranging from ambient pressure to 68 MPa, by using the apparatus shown in Figure 1.

The equilibrium cell, made of stainless steel type-316, has an internal volume of 50 cm^3 and is equipped with two glass windows. The vapor and liquid phases of the cell are circulated to obtain a rapid equilibration by using the magnetically operated pumps. Equilibrium is usually obtained in about 10 min. As shown in Figure 1, the vapor phase is drawn from the top of the cell and returns through the bottom right port, bubbling through the liquid phase. The liquid phase leaves the cell at the bottom and enters through the port at the top right.

Vapor and liquid samples can be injected directly into a Hewlett-Packard gas chromatograph through sampling valves. A Rheodyne six-port sampling valve with an external sampling loop of 20 μL is used to sample the vapor phase. The liquid sampling valve is another Rheodyne six-port valve with an internal loop disk volume of 1 μL. The vapor and liquid samples are transported from the sampling valves to the gas chroma-

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