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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

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The solubility of α-$CaSO_4\cdot 0.5H_2O$ was measured in concentrated phosphoric acid solutions containing approximately 40, 45, 50, and 55% P_2O_5 at 80, 90, 100, and 110 °C, respectively. The weight percent solubility in terms of anhydrous calcium sulfate is given by the equation $\% \; CaSO_4 = 2.879\,181\,03 + 0.013\,992\,58t - 0.089\,429\,39(\% \; P_2O_5) + 0.000\,596\,58(\% \; P_2O_5)^2 - 0.000\,118\,50t(\% \; P_2O_5)$, where t is the temperature (°C) and ($\% \; P_2O_5$) is the weight percent phosphorus pentoxide in solution. The endothermic heat of solution at saturation is found to increase with increasing acid concentration.

Introduction

The production of wet-process phosphoric acid by hemihydrate procedures involves the reaction of sulfuric acid with phosphate rock (depicted as fluorapatite) to produce phosphoric acid, hydrofluoric acid, and sparingly soluble calcium sulfate hemihydrate:

$$10H_2SO_4 + Ca_{10}(PO_4)_6F_2 \xrightarrow{H_2O} 6H_3PO_4 + 2HF + 10CaSO_4\cdot 0.5H_2O \quad (1)$$

These processes may be distinguished from the more common dihydrate processes in which calcium is crystallized from solution as calcium sulfate dihydrate—commonly referred to as gypsum (*1*, *2*):

$$10H_2SO_4 + Ca_{10}(PO_4)_6F_2 \xrightarrow{H_2O} 6H_3PO_4 + 2HF + 10CaSO_4\cdot 2H_2O \quad (2)$$

The nomenclature of calcium sulfate is somewhat confusing. From the standpoint of phosphoric acid production, only three forms of calcium sulfate need to be considered: dihydrate (gypsum), α-hemihydrate, and anhydrite II (*3*). These are the forms which may be crystallized from aqueous solution. Although other forms such as β-hemihydrate, β-anhydrite III, "dead-burned" gypsum, etc., also apparently exist, they are produced by atmospheric thermal or vacuum dehydration processes (*4*). Henceforth, we will refer to α-$CaSO_4\cdot 0.5H_2O$ and $CaSO_4$-II simply as hemihydrate and anhydrite, respectively.

The ability to crystallize one form of calcium sulfate as opposed to another is largely determined by the concentration (ionic strength) and temperature of the reaction medium. Dahlgren (*3*) used the thermodynamic data of Kelley et al. (*4*) to determine the regions of stability and quasi-stability of the crystalline forms of calcium sulfate in phosphoric acid systems. Dahlgren's results are shown in Figure 1. Actually, only two crystalline forms of calcium sulfate are thermodynamically stable in phosphoric acid. Calcium sulfate dihydrate is the stable form at temperatures below about 40 °C and P_2O_5 concentrations below about 38% (region I, Figure 1), while anhydrite ($CaSO_4$) is the stable form at all other attainable regions of the concentration–temperature diagram.

Although thermodynamically unstable, calcium sulfate dihydrate shows a high degree of metastability at higher concentrations and temperatures (region II, Figure 1). At even higher concentrations and temperatures, calcium sulfate dihydrate becomes unstable with respect to the crystallization of metastable calcium sulfate hemihydrate (region III, Figure 1). The rectangular areas of Figure 1 denote the approximate operating ranges of current dihydrate (DH) and hemihydrate (HH) processes, respectively. Hence, both processes actually operate under conditions which produce metastable crystalline phases. The high degree of metastability of dihydrate and hemihydrate apparently results from the high activation energy required for the nucleation of anhydrite (1).

Notwithstanding their potential for producing more concentrated phosphoric acid, filtration, scaling, and corrosion problems have prevented hemihydrate processes from becoming widely accepted (*5*). However, it is believed that the long-term increase in energy cost will favor further development of this technology.

Thus far, there is only a limited amount of available information concerning the metastable solubility of calcium sulfate hemihydrate in phosphoric acid under conditions relevant to hemihydrate processes. The most often cited work is that of Taperova (*6*) and Taperova and Shul'gina (*7*) conducted in the 1940s. However, these investigations only extended up to 90 °C and to a P_2O_5 concentration of 50%. At 80 °C, the highest P_2O_5 concentration was only 42%. In 1967, Shpunt et al. (*8*) extended the 80 °C data up to 50% P_2O_5.

The only other reference is the work of Laptev et al. (*9*) entitled "Solubility of Anhydrous and Semihydrated Calcium Sulfate in Phosphoric Acid Having a 45–54% Phosphorus Pentoxide Concentration at 80–120 Deg." However, we were unable to obtain a copy of this publication.

We now report the results of our investigation of the metastable solubility of α-calcium sulfate hemihydrate in phosphoric acid at concentrations of 40, 45, 50, and 55% P_2O_5 and temperatures of 80, 90, 100, and 110 °C.

Experimental Section

Calcium sulfate hemihydrate (α form) was prepared by digesting 205-g batches of calcium sulfate dihydrate powder (Baker analyzed reagent, 99.9%) in 1000 mL of 6 M $Ca(NO_3)_2$ solution at 75 °C for a period of about 3 days. The crystals then were filtered, washed thoroughly with acetone, and oven dried at 45 °C for 1 h. The crystals were well formed as hexagonal rods ranging in size from about 20 × 60 to 75 × 230 μm. Their identity was established by both polarized light microscopy and X-ray diffraction (XRD) procedures.

The crystals then were subjected to dry sieve analysis. Those in the size range <90 to ≥63 μm were selected for the solubility studies. Chemical analysis gave 27.53% Ca, 65.8% SO_4, 0.06% NO_3, and 6.61% H_2O (calculated: 27.61% Ca, 66.18% SO_4, and 6.20% H_2O). Hence, the apparent molecular composition of the crystals was $Ca(SO_4)_{0.997}(NO_3)_{0.001}(H_2O)_{0.534}$ (ratio SO_4:Ca = 0.997).

The phosphoric acid employed was Baker analyzed reagent (lot No. 0260-3, 85.8% H_3PO_4). Chemical analysis showed it to contain 61.97% P_2O_5, 3 ppm Ca, and <10 ppm SO_4. Stock solutions containing 40.00, 45.00, 50.00, and 55.00% P_2O_5 were prepared by carefully weighing the appropriate quantities

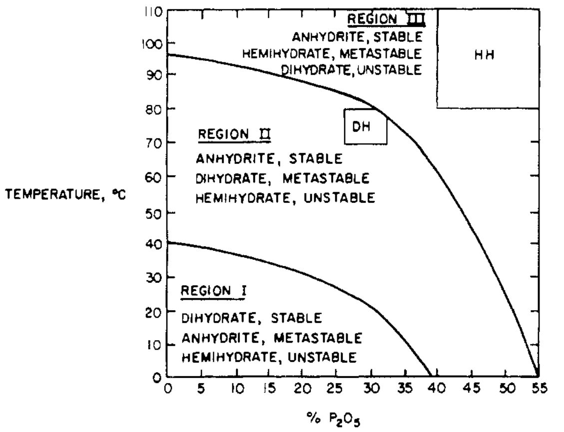

Figure 1. Regions of stability of calcium sulfate in phosphoric acid.

of phosphoric acid and distilled water into 1-L flasks, which then were tightly sealed.

Initial dissolution rate studies were conducted in a three-neck, 250-mL Pyrex flask. The center neck of the flask was equipped with a ground glass sleeve to allow the passage of a lubricated ground glass stirrer rod fitted with a Teflon paddle (2.25 in, circular sector, stirring speed 135 rpm). One side neck of the flask was equipped with a glass sampling well fitted at the bottom with a medium coarse glass frit. The sampling well was capped at the top by means of a ball joint. The remaining neck of the flask was used for reagent addition and was tightly capped by means of a ground glass stopper.

The reaction flask was mounted in a 20-L paraffin oil bath. The bath was heated and stirred by means of a Thermomix 1480 stirrer-regulator. (Use of trade names does not constitute a TVA endorsement.) The temperature was measured with an Ertco mercury thermometer (calibrated against standards certified by the National Bureau of Standards, standard serial No. 48511, NBS identification No. 92564).

The initial experiments were conducted by adding 200 mL of the desired phosphoric acid solution to the reaction flask and allowing the solution to stir for a period of 1 h to establish temperaure equilibrium. Ten grams of calcium sulfate hemihydrate then was admitted. Sampling was conducted with a 1-mL pipet by forcing solution into and out of the sampling well by means of a rubber suction bulb. Sampling generally was conducted as rapidly as possible (approximately 3-min time intervals) during the first 30 min and at longer time intervals thereafter. Crystals were periodically removed and examined under the microscope to ensure that conversion to other crystalline forms had not occurred. At longer reaction times, it was found that identical solubility results could be obtained by turning off the stirrer motor, allowing the crystals to settle to the bottom, and sampling the clear supernatant liquid above them.

Since equilibrium was established quite rapidly (within 3 min), the remaining solubility studies were conducted as follows. Calcium sulfate hemihydrate (2.5 g) was added to each of four 50-mL volumetric flasks. Forty milliliters of 40, 45, 50, or 55% P_2O_5 solution then was pipeted into the respective flasks, which then were placed in the paraffin oil bath at the desired temperature. The solutions were swirled periodically. The crystals then were allowed to settle to the bottom, and the supernatant liquid was sampled after the desired equilibration time (equilibration times: 80 °C, 1 and 3 h; 90 °C, 1 and 3 h; 100 °C, 1 and 2 h; 110 °C, 0.5 and 1.5 h). The crystals were filtered, washed with acetone, and dried. Microscopic and X-ray examination showed that the crystals were still in the form of calcium sulfate hemihydrate.

Solubilities were determined by sulfate analysis of the diluted, saturated solutions using a Dionex Model 2210 ion chromatograph equipped with a Dionex HPLC-AS4 high-efficiency anion separator column. The ion chromatograph was calibrated by preparing standard solutions of $CaSO_4$ (Baker analyzed reagent, $CaSO_4 \cdot 2H_2O$, powder, 99.9%) in 40% P_2O_5 phosphoric acid.

The equilibrium P_2O_5 concentrations were corrected for the calcium sulfate hemihydrate dissolved in the respective solutions.

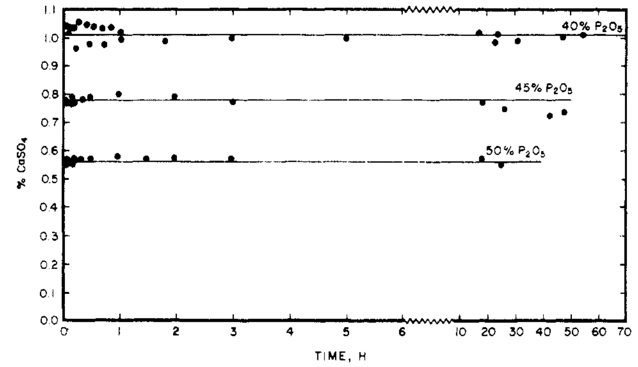

Figure 2. Solubility of α-$CaSO_4 \cdot 0.5H_2O$ in 40, 45, and 50% P_2O_5 solutions at 80 °C as function of time.

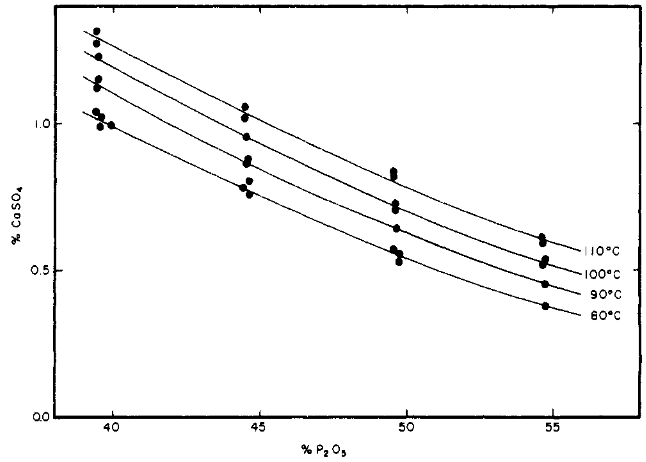

Figure 3. Solubility of α-$CaSO_4 \cdot 0.5H_2O$ in phosphoric acid at 80, 90, 100, and 110 °C.

Results and Discussion

As mentioned previously, calcium sulfate hemihydrate actually is only metastable under the reaction conditions generally employed for the production of phosphoric acid. For this reason, initial experiments were conducted to determine the rate of dissolution of hemihydrate and to ensure that conversion to the more stable (less soluble) anhydrite did not occur during the equilibration periods. The results of these initial kinetic experiments are given in Table I (experiments B, C, D, and E) and shown graphically in Figure 2. As seen in Figure 2, equilibrium is established quite rapidly (within about 3 min) and there is no reduction in solubility over time periods up to about 70 h. However, it was found that if the experiments were allowed to continue, a gradual drop in solubility began to occur and small crystals of anhydrite appeared in the solutions. In 40% P_2O_5 acid at 80 °C, over 250 h was required for the complete conversion of hemihydrate to anhydrite.

The weight percent solubilities (as $CaSO_4$) of α-$CaSO_4 \cdot 0.5H_2O$ in approximately 40, 45, 50, and 55% P_2O_5 phosphoric acids at 80, 90, 100, and 110 °C are given in Table I and shown graphically in Figure 3. The solubility of hemihydrate was found to increase with increasing temperature, but to decrease with increasing P_2O_5 concentrations.

It is of interest to compare our results with the previously obtained data of Taperova (*6*) at 80 °C. The results are shown

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

expt	temp, °C	time, h	% P_2O_5	% $CaSO_4$	K_{sp}, %
40-80-1	80 ± 0.05	1.2	39.58	0.987 ± 0.030	0.202 ± 0.012
40-80-5		3.4	39.57	1.015 ± 0.046	0.214 ± 0.019
B		0.25-71.4	39.97	0.990 ± 0.023	0.204 ± 0.009
C		0.05-24.4	39.46	1.032 ± 0.023	0.221 ± 0.010
45-80-2		1.2	44.62	0.798 ± 0.043	0.132 ± 0.014
45-80-6		3.4	44.64	0.762 ± 0.038	0.121 ± 0.012
D		0.07-18.7	44.51	0.782 ± 0.017	0.127 ± 0.006
50-80-3		1.2	49.72	0.532 ± 0.018	0.0588 ± 0.0040
50-80-7		3.4	49.71	0.542 ± 0.017	0.0622 ± 0.0039
E		0.04-18.5	49.57	0.563 ± 0.021	0.0658 ± 0.0049
55-80-4		1.2	54.78	0.375 ± 0.013	0.0292 ± 0.0020
55-80-8		3.4	54.78	0.376 ± 0.011	0.0294 ± 0.0017
40-90-1	90 ± 0.05	1.2	39.51	1.140 ± 0.034	0.270 ± 0.016
40-90-5		3.2	39.52	1.123 ± 0.033	0.262 ± 0.015
45-90-2		1.2	44.59	0.868 ± 0.023	0.157 ± 0.008
45-90-6		3.2	44.59	0.864 ± 0.023	0.155 ± 0.008
50-90-3		1.2	49.66	0.640 ± 0.027	0.0851 ± 0.0072
50-90-7		3.2	49.66	0.642 ± 0.026	0.0856 ± 0.0069
55-90-4		1.2	54.74	0.450 ± 0.013	0.0421 ± 0.0024
55-90-8		3.2	54.74	0.450 ± 0.013	0.0421 ± 0.0024
40-100-1	100 ± 0.05	1.0	39.48	1.218 ± 0.039	0.308 ± 0.020
40-100-5		2.1	39.48	1.218 ± 0.039	0.308 ± 0.020
45-100-2		1.0	44.54	0.956 ± 0.044	0.190 ± 0.017
45-100-6		2.1	44.54	0.957 ± 0.026	0.190 ± 0.010
50-100-3		1.0	49.62	0.718 ± 0.024	0.107 ± 0.007
50-100-7		2.1	49.62	0.708 ± 0.026	0.104 ± 0.008
55-100-4		1.0	54.69	0.526 ± 0.018	0.0575 ± 0.0039
55-100-8		2.1	54.70	0.521 ± 0.017	0.0564 ± 0.0037
40-110-1	110 ± 0.1	0.5	39.45	1.278 ± 0.059	0.339 ± 0.031
40-110-5		1.5	39.44	1.307 ± 0.044	0.355 ± 0.024
45-110-2		0.5	44.50	1.048 ± 0.037	0.228 ± 0.016
45-110-6		1.5	44.51	1.022 ± 0.033	0.217 ± 0.014
50-110-3		0.5	49.57	0.811 ± 0.041	0.137 ± 0.014
50-110-7		1.5	49.57	0.816 ± 0.031	0.138 ± 0.011
55-110-4		0.5	54.66	0.591 ± 0.027	0.0726 ± 0.0066
55-110-8		1.5	54.65	0.603 ± 0.025	0.0755 ± 0.0063

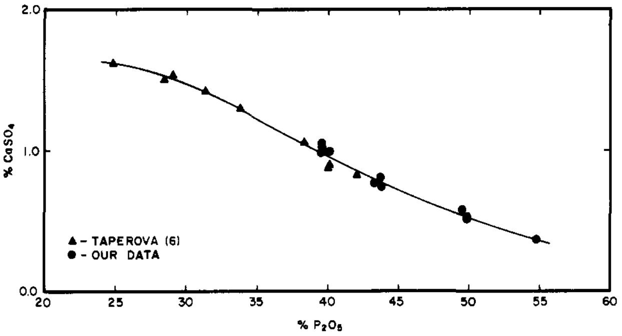

Figure 4. Solubility of α-$CaSO_4 \cdot 0.5H_2O$ in phosphoric acid at 80 °C.

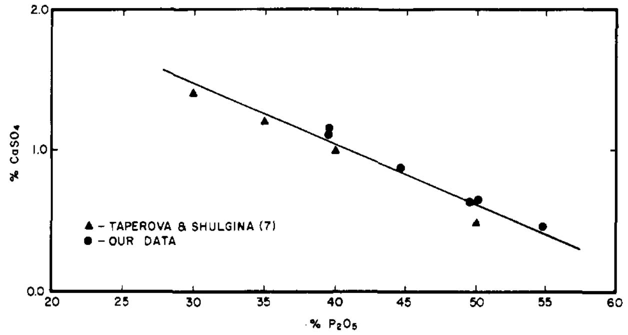

Figure 5. Solubility of α-$CaSO_4 \cdot 0.5H_2O$ in phosphoric acid at 90 °C.

in Figure 4. Our data clearly lie on a smooth extension of the results obtained by Taperova at lower P_2O_5 concentrations. Figure 5 gives a similar comparison with the results of Taperova and Shul'gina (*7*) at 90 °C. Again, good agreement between the two sets of data was obtained.

Multiple regression techniques were used to correlate the solubility of α-$CaSO_4 \cdot 0.5H_2O$ (Table I) with weight percent P_2O_5 concentrations (% P_2O_5) and equilibration temperature (t), °C. The weight percent solubility (as $CaSO_4$) is well expressed by the equation

$$\% \ CaSO_4 = 2.87918103 + 0.01399258t - 0.08942939(\% \ P_2O_5) + 0.00059658(\% \ P_2O_5)^2 - 0.00011850t(\% \ P_2O_5)$$

correlation coefficient $R^2 = 0.998$

coefficient of variation CV = 1.57 (3)

This equation may be used to accurately estimate the solubility of α-$CaSO_4 \cdot 0.5H_2O$ within the experimental range 40-55% P_2O_5 and 80-110 °C, but should not be used for extrapolations outside this range.

Moderate extrapolations of the data may be made using the van't Hoff equation

$$\ln \% \ CaSO_4 = (-\Delta H/RT) + C \qquad (4)$$

where ΔH is the apparent heat of solution at saturation, T is the absolute temperature (K), R is the gas constant (1.987 cal K^{-1} mol^{-1}), and C is an integration constant (*10*). Hence, Figure 6 gives van't Hoff plots of the solubility of α-$CaSO_4 \cdot 0.5H_2O$ in 40, 45, 50, and 55% P_2O_5 phosphoric acid solutions as calculated from eq 3. The derived van't Hoff parameters are given in Table II. The apparent endothermic heat of solution of α-$CaSO_4 \cdot 0.5H_2O$ is seen to increase from 2.2 to 4.3 kcal/mol as the concentration of P_2O_5 increases from 40 to 55%.

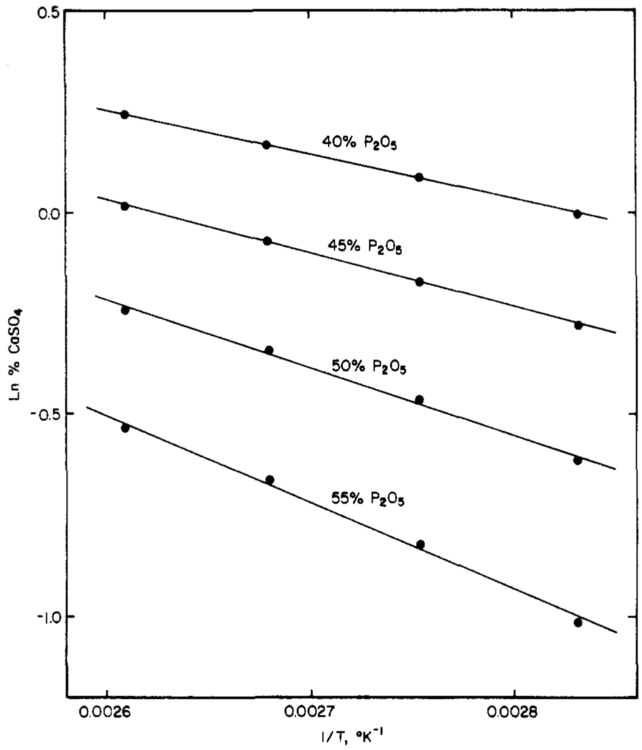

Figure 6. ln % $CaSO_4$ versus $1/T$ for 40, 45, 50, and 55% P_2O_5 solutions.

Table II. van't Hoff Parameters Associated with Weight Percent Saturation of α-$CaSO_4\cdot 0.5H_2O$ in Concentrated Phosphoric Acid

% P_2O_5	ΔH, cal/mol	C	R^{2a}
40	2201.9 ± 19.1	3.135 ± 0.002	0.999
45	2648.2 ± 36.9	3.496 ± 0.003	0.999
50	3295.4 ± 70.9	4.092 ± 0.006	0.999
55	4307.7 ± 143.7	5.134 ± 0.012	0.998

[a] Correlation coefficient for fit of data to eq 3.

The solubility data also may be used to determine the apparent weight percent solubility product constants (column 6, Table I) for α-$CaSO_4\cdot 0.5H_2O$ in concentrated phosphoric acid, as defined by the equation

$$K_{sp} = (\%\ Ca)(\%\ SO_4) = 0.20773(\%\ CaSO_4)^2 \qquad (5)$$

Regression of the data in terms of temperature (t), °C, and P_2O_5 concentration (% P_2O_5) gives the equation

$$K_{sp} = 1.04058881 + 0.01194334t - 0.05323702(\%\ P_2O_5) + 0.00059789(\%\ P_2O_5)^2 - 0.00019269t(\%\ P_2O_5)$$

$$\text{correlation coefficient} \quad R^2 = 0.998$$

$$\text{coefficient of variation} \quad CV = 3.21 \qquad (6)$$

Again, the equation should only be used within the range of the experimental variables (40-55% P_2O_5 and 80-100 °C). Moderate extrapolations may be made using the van't Hoff relationship.

Glossary

R^2	correlation coefficient
CV	coefficient of variation
ΔH	apparent heat of solution at saturation
T	absolute temperature, K
R	gas constant, 1.987 cal K^{-1} mol^{-1}
C	integration constant
K_{sp}	solubility product constant, $(\%)^2$

Registry No. H_3PO_4, 7664-38-2; $CaSO_4\cdot 0.5H_2O$, 10034-76-1.

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Solution Thermodynamics of First-Row Transition Elements. 1. Apparent Molal Volumes of Aqueous $NiCl_2$, $Ni(ClO_4)_2$, $CuCl_2$, and $Cu(ClO_4)_2$ from 15 to 55 °C

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We have used a flow densimeter to measure the densities of aqueous solutions of $NiCl_2$, $Ni(ClO_4)_2$, $CuCl_2$, and $Cu(ClO_4)_2$ at 10 °C intervals from 15 to 55 °C. Infinite dilution apparent molal volumes are determined at each temperature by using the Redlich-Meyer equation. These values are fitted to the polynomial $\phi_v^0 = a + bt + ct^2$. The Pitzer formalism has been used to fit the volume data over the entire concentration range (0-3.5 m).

Introduction

There are many practical situations in which it is desirable to know the densities of electrolyte solutions and how these densities are affected by changes in temperature. For example, there is a growing interest in the properties of concentrated electrolyte solutions and their application to industrial processes, the chemistry of geothermal brines, and oil well completion.

Most volume work has been done on solutions of single

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