Transient Solubilities in the Calcium Sulfate–Water System

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The change in solubility in water with time of α and β calcium sulfate hemihydrate and of β-soluble anhydrite and "insoluble" anhydrite were determined over the temperature range of 35° to 110° C. The solubility of the hemihydrates goes through a maximum with time, which is related to modifications in the calcium sulfate phase present. The α-hemihydrate is less soluble but more stable than the β form. The stability of α and β hemihydrate increase as the transition temperature, 99° C. for gypsum-α-hemihydrate and 103° C. for gypsum-β-hemihydrate, is approached. At temperatures above 45° C. the solute content in contact with "insoluble" anhydrite, prepared by igniting gypsum at 890° C., surprisingly increased with time well beyond the values previously reported for anhydrite solubility.

THREE FORMS of calcium sulfate have long been recognized, $CaSO_4 \cdot 2H_2O$ (gypsum), $CaSO_4 \cdot \frac{1}{2}H_2O$ (hemihydrate), and $CaSO_4$ (anhydrite). Various modifications of these forms have also been postulated, but after a careful study and review of previous work, Kelley, Southard and Anderson (*9*) in 1941 concluded that the only unique and reproducible forms were: $CaSO_4 \cdot 2H_2O$, α-$CaSO_4 \cdot \frac{1}{2}H_2O$, β-$CaSO_4 \cdot \frac{1}{2}H_2O$, α- and β-soluble anhydrites, and insoluble anhydrite. The α-hemihydrate is prepared, for example, by dehydration of gypsum in an atmosphere of saturated steam. The β-hemihydrate is formed by dehydration of gypsum under a lower water vapor pressure, and it shows a higher solubility than the α-hemihydrate. α- and β-anhydrites are prepared by further dehydration of α- and β-hemihydrates, respectively; both rehydrate fairly readily. Insoluble anhydrite, on the other hand, is reported to be stable above 40° C., in the sense that it does not hydrate.

Solubility data for calcium sulfate in water have been reported by many investigators. Most of the results are grouped together in Figure 1. Solubility data on $CaSO_4$ as "insoluble anhydrite" and on $CaSO_4 \cdot 2H_2O$ show good agreement between different investigators. Date on hemihydrate at temperatures below about 120° C., however, show more discrepancies. Ridell (*13*), quoted by Kelley and Southard, reported the solubilities of α-hemihydrate shown by the lower of the two similar lines on Figure 1. A few studies by him on β-hemihydrate showed solubilities from 22 to 5 per cent higher than for α-hemihydrate, from which Kelley and Southard concluded that the earlier investigators who reported higher solubilities may have worked with samples containing β-hemihydrate or β-soluble anhydrite.

Since the comprehensive review by Kelley, Southard, and Anderson (*9*), the only other solubility studies in pure water have been those of Sborgi and Bianchi (*14*), Dickson, Blount, and Tunell (*4*), and Booth and Bidwell (*1*). Under thermodynamically favorable conditions the hemihydrates and soluble anhydrites rapidly hydrate, whereas the insoluble anhydrite does so only very slowly. Budnikov and Kosyreva, (*2*) showed that the rate of hydration of β-hemihydrate in a water vapor atmosphere and in water at room temperature and the rate of its dissolution are much faster than those for α-hemihydrate, but no quantitative information has been published on the rates of these phase transformations or associated solubility effects. Calcium sulfate is the most troublesome compound in causing scale formation, as in saline water conversion plants. The rate of phase transformations together with accompanying transient solubilities can have a profound effect on scale formation and behavior. The purpose of these studies was to determine the rates of some of these phase transformations, the transient solubilities accompanying them and the factors affecting them. The results also clarify our knowledge concerning the solubilities of α- and β-hemihydrates. The study covered the temperature range from 25° to 110° C.

EXPERIMENTAL

Calcium Sulfate Modifications. Table I gives the modifications of calcium sulfate and its hydrates used in the study, together with their method of preparation, determined water content, and x-ray characteristics. Distilled water with a maximum conductivity of three micromhos/cm. at 25° C. was the solvent.

Experimental Method. The solubility measurements were carried out in a four-necked, one-liter borosilicate glass flask held in a constant-temperature bath, equipped with a glass stirrer (260 r.p.m.), a thermometer, a sampling tube, and a conductivity cell.

The constant-temperature bath was a 10-gallon oil bath equipped with stirrer, fixed heater, and intermittent heater controlled by a mercury regulator. The bath temperature was held to ±0.05° C. at 25° C. and ±0.1° C. at 95° C.

A filter containing tightly packed borosilicate glass fiber was attached to the immersed end of the sampling tube, and samples of the solution were removed by suction into a tared sample test tube contained inside a suction flask. To eliminate evaporation losses, the suction flask containing the sample test tube was filled with ice water and the suction was limited to 160 mm. of Hg by a manostat. Samples of the solid phase were obtained by rapidly filtering about 40 ml. of the slurry through a tared Gooch crucible.

Table I. Calcium Sulfate Modifications

Name, Formula	Method of Preparation	Water Content	X-ray Diffraction Pattern
Gypsum $CaSO_4 \cdot 2H_2O$	J.T. Baker Analytical Grade, slurried with water and filtered before use	20.9% (Stoichiometric is 20.9%)	Excellent agreement with ASTM card No. 6-0046 for gypsum (Monoclinic)
α-Hemihydrate $\alpha\text{-}CaSO_4 \cdot \frac{1}{2}H_2O$	Gypsum-water slurry heated at 115° C. for three days, filtered, dried at 70-75° C. in oven purged with air saturated with water vapor at 25° C. Stored over Drierite.	6.0% (Stoichiometric is 6.2%)	Reasonable agreement with ASTM card No. 2-0675 for $CaSO_4 \cdot \frac{1}{2}H_2O$ (Plaster of Paris) (Hexagonal). Average crystallite size about 0.3 micron.
β-Hemihydrate $\beta\text{-}CaSO_4 \cdot \frac{1}{2}H_2O$	Gypsum heated for seven days at 70-75° C. while flushing with air saturated with water vapor at 25° C. Stored over Drierite	6.2%	Pattern differs from that of α-hemihydrate only in that the average crystallite size (about 0.09 micron) is smaller.
β-Soluble Anhydrite $\beta\text{-}CaSO_4$	Gypsum heated for two days at 110° C.	0.2%	Some pattern as β-hemihydrate.
Insoluble Anhydrite $CaSO_4$	Gypsum heated for 19 hours at 890° C.	0.0%	Excellent agreement with ASTM card No. 6-0226 for anhydrite (orthorhombic)

The solid was immediately washed with 25 ml. of anhydrous ethanol under suction to remove adherent water.

Factory certified thermometers, calibrated in 0.1° intervals, were used to determine oil bath temperatures and to calibrate thermometers immersed in the calcium sulfate slurries.

Solubility measurements were made starting with either distilled water or with a solution saturated at room temperature with gypsum and filtered to remove all solid. In a typical experiment, the mixing flask was charged with 600 ml. of water or the saturated gypsum solution and allowed to come to bath temperature. A charge of five grams of calcium sulfate was stirred into the water or solution. Rapid solubility changes were followed by conductivity measurements, and samples of the solution and solid phase were taken regularly for analysis.

For determining solubilities at temperatures in the 100° to 115° C. range, a closed glass vessel assembled from heavy-walled borosilicate glass fittings was used. The vessel had a four-necked head through which a thermometer, a slurry sampling tube, an internal filtering tube, a conductivity dip cell, and connections for a nitrogen inlet, a pressure gauge, and a mercury manostat were inserted. The contents were heated by a mantel and stirred by a magnetic stirring bar. Temperature of the slurry was controlled by allowing the liquid to gently boil at a controlled nitrogen pressure. By carefully adjusting the heat load and the manostat, temperatures were controlled to ±0.2° C.

Analytical Method. The solutions were analyzed for calcium by the ethylene diamine tetraacetic acid (EDTA) method (*16*) and for sulfate by the method of Fritz and Yamamura (*5*).

The titer of the EDTA solution was determined by titrating weighed samples of primary grade calcium carbonate, which had been dried at 285° C. All solubilities are reported as parts of $CaSO_4$ per million of water, based on calcium analysis. Occasional sulfate analyses of solids and pH measurements of slurries were made to check for acid or basic salt formation.

The hydrate water content of calcium sulfate was determined gravimetrically according to ASTM procedure C471-61. After washing the solid on the filter with ethanol, it was dried for two hours at 45° C. and then weighed. It was then ignited in a muffle furnace for one hour at 400° C. and reweighed. The weight loss was taken as the bound water content. Specific conductivities were determined by immersing a dip-type conductivity electrode into the slurry and measuring the resistance with a 1000-cycle bridge (Industrial Instruments Model RC-16B2). Specific conductivities were correlated with calcium sulfate content and solution temperature by analysis of various filtered solutions by the EDTA method. Conductivities were used principally to locate solubility maxima, and exact calcium contents were determined by EDTA titrations.

RESULTS

In the temperature range studied (25° to 110° C.), the characteristic solubility of gypsum was attained within a fraction of a minute after the salt was agitated with water or with presaturated solution. Our measured solubilities (Table II) agreed closely with those previously reported, as shown in Figure 1. When α- or β-hemihydrate or β-soluble anhydrite was slurried with water, however, the conductivity rose abruptly to a value substantially exceeding the solubility of gypsum, and then decreased and asymptotically approached the conductivity of the saturated gypsum solution. The solid line on Figure 2 shows a typical transient solubility curve when β-soluble anhydrite is slurried in water at 35° C. The dashed line on Figure 2 shows the increase in solubility stability when the solid phase was removed by filtration two minutes after the initial contacting of the solid phase with water. On the other hand, seeding the slurry with two grams of gypsum crystals one minute after solid and water were contacted caused the solute content to drop more quickly as shown by the dotted line on Figure 2. The hemihydrates and soluble anhydrites are known to be unstable forms under these conditions, and it appears that the mechanism of change involves primarily solution of the hemihydrate or anhydrite form and precipitation of the dihydrate (gypsum) form. The solute content in the solution at any given moment is determined by the relative rates of these two processes. Increasing the initial charge of β-soluble anhydrite from five grams to 10 grams had no significant effect on the solubility curve.

A series of studies over the 35° to 93° C. temperature range with β-soluble anhydrite is shown in Figure 3a. Figure 3b shows the corresponding change in hydrated water content of the solid phase at three of the temperatures: 45°, 65°, and 84° C. Note that a sharp decrease in solute content takes place when the solid sample is practically completely converted to gypsum. This is consistent with the above solution-precipitation mechanism. Within the limits of experimental error, β-hemihydrate and β-soluble anhydrite showed identical transient solubility behavior, indicating that the hydration of β-soluble anhydrite to β-hemihydrate is a much faster process than the further hydration of β-hemihydrate to gypsum.

The transient solubility behavior of the α- and β-hemihydrate modifications is compared in Figures 4, 5, and 6 at 45°, 65°, and 84° C., respectively. It can be seen that the transient solubility maximum of β-hemihydrate is

Table II. Solubility of Calcium Sulfate in Water

Temp., °C.	Solubility (Parts by Weight of $CaSO_4$ per Million of Water)				
	Gypsum $CaSO_4 \cdot 2H_2O$	β-Hemihydrate β-$CaSO_4 \cdot \frac{1}{2}H_2O$	β-Soluble Anhydrite β-$CaSO_4$	α-Hemihydrate α-$CaSO_4 \cdot \frac{1}{2}H_2O$	Insoluble[a] Anhydrite ($CaSO_4$)
25	2096 ± 2				2610
35	2120 ± 3	6712 ± 93	6819		2310
40					2160
45	2098 ± 7	6050	5975	4552	2000
55	2064 ± 3				
60		4140 ± 40	4231 ± 129		
65	1997 ± 3	3780		3280	1405
75	1925 ± 6				
80		2745	2796 ± 16		
84		2515	2506	2380	
85	1825 ± 7				980
93		2170 ± 50	2110 ± 10		
95	1724 ± 4				
100	1660	1727 ± 21	1767		
105	1635	1601 ± 9	1605	1499	
110	1584	1546	1505		
115	1540 ± 3				

[a] Extrapolated to zero time.

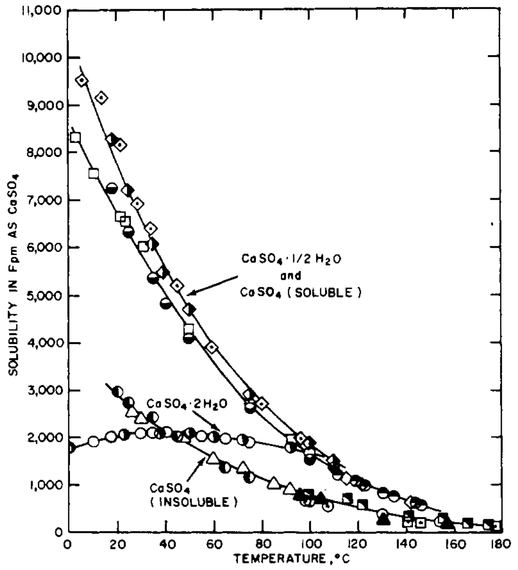

Figure 1. Solubility of calcium sulfate

$CaSO_4 \cdot 2H_2O$	DATE	REFERENCE
◑ POSNJAK	1938	12
○ HULETT and ALLEN	1902	8
$CaSO_4 \cdot 1/2\,H_2O$		
□ RIDDELL	1941	13
◆ SBORGI and BIANCHI	1940	14
◇ CHASSEVENT	1926	3
● PARTRIDGE and WHITE	1929	11
$CaSO_4$ ("SOLUBLE")		
⊖ SBORGI and BIANCHI	1940	14
◇ HALL, ROBB, and COLEMAN	1926	6
$CaSO_4$ ("INSOLUBLE")		
▲ DICKSON, BLOUNT, and TUNELL	1963	4
⊡ BOOTH and BIDWELL	1950	1
△ POSNJAK	1938	12
◐ HILL	1937	7
⊙ PARTRIDGE and WHITE	1929	11

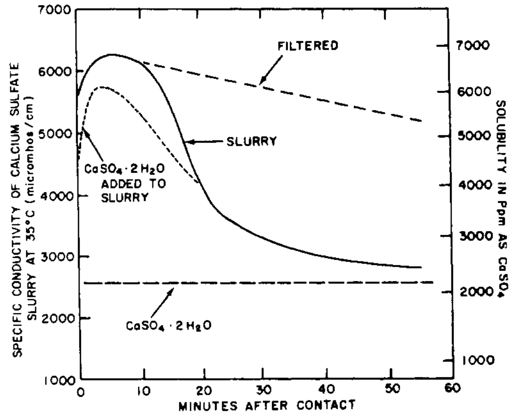

Figure 2. Transient solubility of β-soluble anhydrite in water at 35° C.

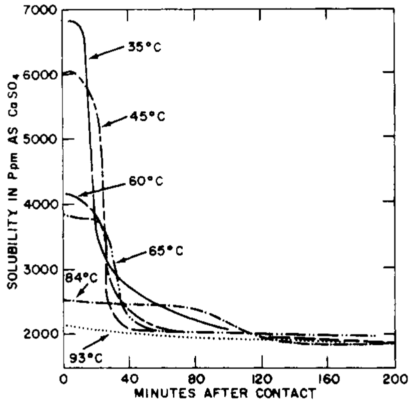

Figure 3a. Transient solubility of β-$CaSO_4$ in water

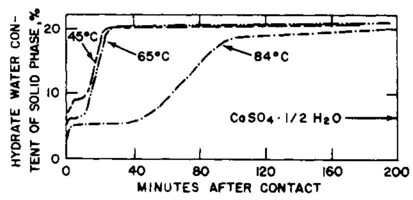

Figure 3b. Hydrate water content of solid phase

always higher and decreases much faster than does that of α-hemihydrate. These figures and Figure 3 show that the time required for conversion to gypsum grows longer as the temperature is increased. This is again consistent with the solution-reprecipitation mechanism in which the rate would be expected to be proportional to the difference in solubilities of the two phases. At 93° C., the conductivities of β-hemihydrate and β-soluble anhydrite slurries were the same and remained almost unchanged over a 60-minute period with no transients at a value corresponding to a solute content of 2120 p.p.m. of $CaSO_4$. This is about 15% above the solubility of gypsum at this temperature. Solubility maxima are tabulated in Table II.

Sborgi and Bianchi and Chassevent both measured solubilities by an electrical conductivity method and took the maximum value they found as the solubility. In Sborgi and Bianchi's work from five to 15 minutes were required for the maximum to be reached, but there was no correlation between the temperature and the time required for this to happen. No flat maxima were observed except for one run with anhydrite at 110° C. Chassevent did not report the times for his maxima to be reached although some sample runs indicated they were roughly of the same duration. Since solution and reprecipitation are occurring simultaneously, the true solubility could conceivably exceed this maximum in some cases. If the maximum is represented by a flat plateau this can be reasonably taken as the true solubility of the hemihydrate form. This was the case in our work at all temperatures of 60° C. and higher. At lower temperatures a greater scatter was observed in the maxima in repeated runs.

X-ray diffraction patterns for α- and β-hemihydrates differ only in that the size of the average crystallite of the α form (about 0.3 micron) was greater than that of the β form (about 0.09 micron). This agrees with a similar conclusion of Budnikov and Kosyreva (2). BET surface areas of the two materials were 4.6 m.^{2}/gram for the α form and only slightly larger (5.9 m.^{2}/gram) for the β form. Apparently the greater instability of the β-hemihydrate is associated with a higher energy content rather then greater exposed surface area. To determine if particle size might account for the difference in the solubility effects between α- and β-hemihydrate, a sample of α-hemihydrate was ground in a ball mill for 24 hours before determining the solubility indicated by the dot-dash curve of Figure 4. The transient solubility peak for the ground sample is sharper than for the unground sample, and the maximum solubility is slightly lower, indicating that particle size alone cannot account for the difference between the solubilities of the α- and β-hemihydrates.

The transient solubility maxima as a function of temperature are plotted in Figure 7. The results clearly fall on two separate lines. The solubility data of α-hemihydrate correspond to the data of Sborgi and Bianchi (*14*) for their so-called "soluble anhydrite" and to that of Riddell (*13*) for α-hemihydrate. The experimental results for β-hemihydrate and β-soluble anhydrite correspond to those of Chassevent (*3*) and Sborgi and Bianchi (*14*) for their so-called "hemihydrate". Figure 7 also summarizes our data for gypsum and for insoluble anhydrite. The latter are discussed below.

According to Figure 7, three distinct transition temperatures are present in the $CaSO_4$-H_2O system. Kelley and Southard's calculations of free energy changes accompanying the dissociation of $CaSO_4 \cdot 2H_2O$ into its several dehydration products in the presence of liquid water showed that the only stable substances in the system are $CaSO_4$ (insol.) and $CaSO_4 \cdot 2H_2O$, the former being stable above 40° C. and the latter below this temperature. On Figure 7, two metastable equilibrium points can be located. One represents the equilibrium of $CaSO_4 \cdot 2H_2O$, α-$CaSO_4 \cdot \frac{1}{2}H_2O$, and liquid water. Figure 7 indicates that the trans-

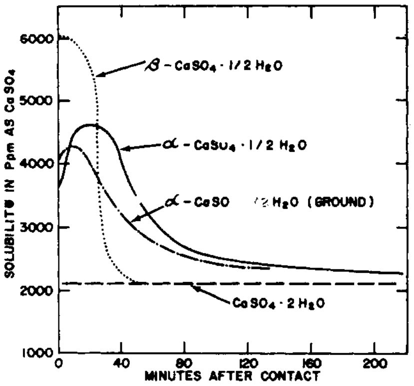

Figure 4. Transient solubility of α- and β-calcium sulfate hemihydrate in water at 45° C.

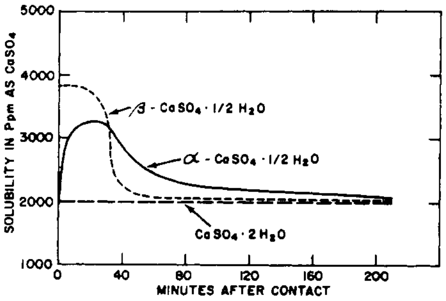

Figure 5. Transient solubility of α- and β-calcium sulfate hemihydrate in water at 65° C.

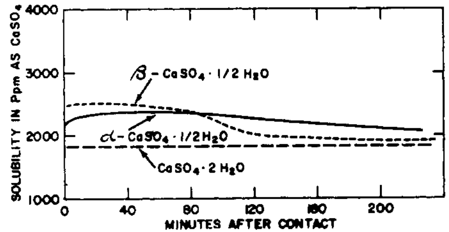

Figure 6. Transient solubility of α- and β-calcium sulfate hemihydrate in water at 84° C.

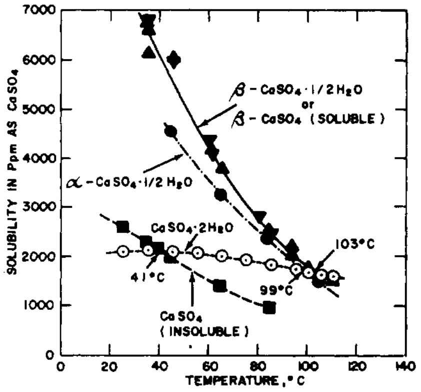

Figure 7. Calcium sulfate solubility in water. All data points refer to present study

ient temperature is 99 ± 1° C. Partridge and White (*11*) reported the intersection of the gypsum-hemihydrate curves to be between 98° and 100° C., and Posnjak (*12*) reported it at 97.5 ± 1° C. A temperature of 97° can be calculated from the free energy equations given by Kelley and Southard (*9*). Dilatometric measurements of Southard (*9*) indicated this temperature to be 100 ± 1° C. Korol'kov and Krupnova (*10*) recently reported the transition temperature to be 102–105° C. and an earlier value of 107.2° C. was obtained with dilatometer measurements by van't Hoff (*15*) and coworkers. These higher transition temperatures are probably associated with the system $CaSO_4 \cdot 2H_2O$-β-$CaSO_4 \cdot \frac{1}{2}H_2O$ and water, which has a transition temperature of 103 ± 1° C., according to the intersection of our solubility curves. Kelley and Southard's free energy data indicate a transition temperature of 131° C. Their free energy data likewise indicate the transition temperature between α- and β-hemihydrate to be 191° C., the α-hemihydrate being the more stable variety at temperatures below 191° C.

A series of solubility determinations were carried out with gypsum at 100°, 105°, and 110° C. in a unit pressurized with nitrogen. At 100° C., no change in water content of the solid phase or in solute content was observed over a 72-hour period. At 105° C., no dehydration was observed over the same time period although the solute content slightly increased. At 110° C. a slow dehydration of gypsum was observed, most probably to the hemihydrate. The soluble anhydrites were hydrated to the corresponding hemihydrates at a fast rate at all these temperatures; the hydration was completed in less than one hour. Both hemihydrates showed no change in water content during a contact time of 48 hours at 100 to 110° C. Slurry conductivity measurements could not be used to determine solubility because of coagulation of the solid phase on the electrodes at 100° C. or above.

Korol'kov and Krupnova (*10*) recently investigated the hydration rate of a hemihydrate which, according to the method of preparation described, was apparently the β-modification. They showed that at 20° C. in contact with water, hydration was completed in 20 minutes, and at 80° C. in about two hours; this agrees fairly closely with our results in Figure 3. They did not study solubilities. The hemihydrate did not recrystallize to dihydrate at 90° and 100° C. in five hours contact time. Their experiments showed that an addition of 2.5–20% gypsum to the hemihydrate sample increased substantially the rate of hydration; at 80° C. the hydration of the mixture was completed in 20 minutes, and at 90° C. the hydration was slower. The conversion of the last 10% of hemihydrate was very slow. At 100° to 102° C. hemihydrate was still hydrated at a gradually decreasing rate with increasing temperature. But, at 105° C., although an initial hydration was observed after 20 minutes, a distinct reversal took place and practically all the solid material recrystallized to hemihydrate in 120 minutes.

All these experimental results clearly show that the transient solubilities in the calcium sulfate–water system are closely related to the different calcium sulfate modifications. Solubility changes follow the recrystallization of initially unstable modifications. This process is controlled by the nucleation and growth rate of the new crystalline form, the driving force for these processes presumably being the solubility difference between the initial and final modifications.

A few experiments were also carried out with insoluble anhydrite over the temperature range of 25° to 95° C. It is known that at these temperatures the solution may not reach saturation for some time. At 25° C., for example, Hill (*7*) reported the solubility at the end of one day to be about 97% of that found at the end of one week. Likewise here the solubility at all temperatures increased with time, as shown on Figure 8, but, especially at temperatures of 45° C., and above, to ultimate solute contents substantially exceeding those previously reported for anhydrite solubility. (The first data point on Figure 8 for each temperature corresponds to one-half hour.) Hill reported solubility data for anhydrite at 35° to 65° C. which were approached from both undersaturation and supersaturation over periods ranging into several months. At 25° to 35° C. our values obtained at about 48 hours slightly exceed his, and our values extrapolated to zero contact time are slightly less than his. Our study showed that the solubility at 65° C. increased substantially with time to a value at the end of 45 hours of 1773 p.p.m. which was still increasing and greatly exceeds the values of 1335 and 1520 p.p.m. reported by Hill at the end of four months, approached from undersaturation and supersaturation, respectively. At 85° and 95° C., the solubility in our studies increased more slowly with time than at 65° C. but continued to do so for days. At 85° C., for example, the solubility had reached 1251 p.p.m. after 165 hours (this datum is not shown on Figure 8) which substantially exceeds Hill's solubility data. The bound water content of the solid phase, originally 0.0%, even after 160 hours of contact with water at 85° C. did not exceed 1%. Apparently a slow change of insoluble anhydrite to some more soluble form is slowly occurring.

The difference in behavior of our insoluble anhydrite and that of Hill may be ascribed to the method of preparation. Hill's was prepared by boiling gypsum in 20% sulfuric acid for three days; ours was prepared by heating gypsum for 19 hours at 890° C. However, Hill's data agree closely with those of Posnjak (*12*) who prepared his anhydrite by heating gypsum to 500° C. Nevertheless, if we take our solubility data for insoluble anhydrite as extrapolated to zero time, our gypsum and insoluble anhydrite solubility curves intersect at 41 ± 1° C., which agrees closely with Hill's curves intersecting at 42° C. Kelley and Southard (*9*), from thermodynamic data, report the transition temperature between gypsum and insoluble anhydrite as 40° C.

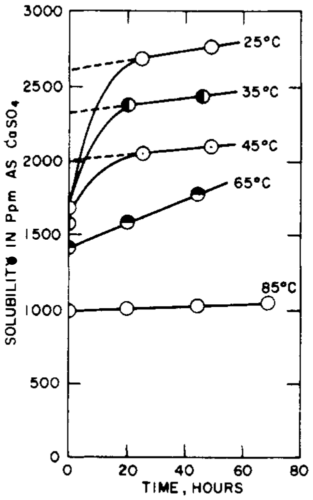

Figure 8. Solubility of insoluble anhydrite in water

ACKNOWLEDGMENT

Solubility measurements and solid phase analyses were made by J.P. DeMonico. X-ray diffraction studies were made by R.R. Ferguson in the Dayton Laboratories of Monsanto Research Corp. Work sponsored by the Office of Saline Water, U.S. Department of Interior, L.E. Leiserson, project monitor.

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RECEIVED for review October 2, 1963. Accepted March 2, 1964.

Viscosities of Binary Mixtures of Benzyl Acetate with Dioxane, Aniline, and *m*-Cresol

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Accurate measurements of viscosity as a function of composition of binary mixtures of benzyl acetate with dioxane, aniline and *meta*-cresol are reported. The data are interpreted in terms of Eyring's relation for the viscosity of pure liquids. The value of the interaction energy W_{visc} is calculated for each of the three mixtures.

THE STUDIES of Moore and Russel (*3*) and Moore and Styan (*4*) on the dielectric constants, volume and heats of mixing on mixtures of benzyl acetate with dioxane, aniline and *meta*-cresol were extended by our studies on surface tensions, boiling points (*2*), and viscosities. A treatment of viscosities of mixtures based on Eyring's (*6*) theory of viscosities of pure liquids, and assuming a regular solution type model for the activation free energy, represented rather well the dependence of mixture viscosities on composition.

EXPERIMENTAL

The purification of these liquids has already been reported elsewhere (*2*). Viscosities of the pure liquids and mixtures at different concentrations were determined at fixed temperatures. The measurements were carried out in an Ostwald viscometer which for aniline gave a time period of flow of 1479.4 seconds. The thermostat bath was controlled to within ±0.01° C. The densities were measured in a previously calibrated pycnometer and were reproducible to ±0.0001 gram/ml. The viscosities reported here are accurate to within 0.5%. The data for the pure liquids are given in the following table.

	Molecular Weight	Density Gram/Ml. (30° C.)	Boiling Point, ° C.	Viscosity cp.
Benzyl Acetate	150.17	1.0482	214.0	1.3525(40° C.)
Dioxane	88.10	1.0232	106.5	0.6256(40° C.)
Aniline	93.12	1.0151	184.5	3.1457(30° C.)
meta-Cresol	108.13	1.0275	194.4	1.0283(40° C.)

RESULTS AND DISCUSSION

Several empirical or semiempirical relations (*5*) have been used to represent the dependence of viscosity on concentration in binary liquid mixtures. Used frequently among them has been the Arrhenius relation:

$$\ln \eta_s = x_1 \ln \eta_1 + x_2 \ln \eta_2 \tag{1}$$

where η_s, η_1, η_2, are the viscosities of the solution; 1 and 2 the viscosities of pure liquids. This represents well the data for nearly ideal binary mixtures but does not represent data for non ideal solutions. The next order of approximation would appear to be a regular solution model. For this purpose Eyring's (*4*) model for the viscosity of a pure liquid:

$$\eta = \left(\frac{\lambda}{\alpha}\right)^2 \frac{hN}{V} e^{f/RT} \tag{2}$$

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