Solubility of Calcium Sulfate Dihydrate and Association Equilibria in Several Aqueous Mixed Electrolyte Salt Systems at 25°C

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Measurements were made of the solubility at 25°C of calcium sulfate dihydrate in the mixed electrolyte systems (*a*) Na_2SO_4–NaCl–H_2O, (*b*) Li_2SO_4–$LiNO_3$–H_2O, and (*c*) Li_2SO_4–LiCl–H_2O for comparison with solubility measurements in Na_2SO_4–$NaNO_3$–H_2O made previously. The proposed association equilibria for calcium sulfate indicate an apparent invariance of activity coefficients for Ca^{2+}, SO_4^{2-}, and $CaSO_4^0$ within a single system at constant ionic strength, *I*. This behavior was observed for all four systems at *I* (molal units) = 0.5, 2, and 6 over a wide range of the ratio, molality of added sulfate/molality of 1–1 electrolyte. An effort is made to account for these unique differences in solubility behavior among the four systems, at both constant ionic strength and molality of SO_4^{2-}, in terms of the amount of "free" or unsolvated water present. The possibility that the actual ionic strength of a solution is less than the formal ionic strength is discussed and qualitatively related to the solubilities. The use of a modified Harned's rule is discussed also, but the rule was not found as convenient for any single system as is the association equilibria approach.

An earlier study (*10*) of the solubility of $CaSO_4 \cdot 2H_2O$ (gypsum) in Na_2SO_4–$NaNO_3$–H_2O solutions, over the temperature range of 0.5–350°C, indicated that the dissolved calcium sulfate was in the form of both ion pairs ($CaSO_4^0$) and ions (Ca^{2+}, SO_4^{2-}). Further, the activity coefficients of the neutral molecule and of the ions remained essentially constant, at each temperature, as the ratio $NaNO_3/Na_2SO_4$ was varied widely at a given ionic strength (*I*, molal units) between 0.5 and 6. A general implication of these results is that the ionic solubility product quotient (Q_{isp}) of $CaSO_4 \cdot 2H_2O$ in aqueous solutions is independent of the nature of dissolved salts present and dependent only upon the ionic strength of the solution. That this may not be the case can be seen by comparing the solubilities of $CaSO_4 \cdot 2H_2O$ in aqueous solutions of various 1–1 strong electrolytes at the same ionic strength and temperature (*8*). The objective of this present investigation was to determine the solubilities and equilibrium quotients of $CaSO_4 \cdot 2H_2O$ at 25°C in Na_2SO_4–NaCl–H_2O, Li_2SO_4–$LiNO_3$–H_2O, and Li_2SO_4–LiCl–H_2O solutions at approximate values of *I* of 0.5, 2, and 6 for comparison and correlation with the experimental results from the system $CaSO_4 \cdot 2H_2O(s)$–Na_2SO_4–$NaNO_3$–H_2O (*10*). The alkali metal sulfates were added to vary the molality of sulfate ion while the 1–1 salts of the corresponding alkali metal were used both to vary the uncommon ion and to adjust the ionic strength to the desired constant value.

EXPERIMENTAL

Reagent-grade chemicals were dried at about 150°C before preparing stock solutions of each with demineralized water. These concentrated stock solutions were diluted quantitatively, when necessary, for experimental use. Treatment of reagent-grade $CaSO_4 \cdot 2H_2O$ before use has been described earlier (*10*). Excess solid $CaSO_4 \cdot 2H_2O$ was equilibrated at 25.0 ± 0.1°C in small polyethylene bottles with the several different mixtures of electrolytes in aqueous solution, each at the same constant ionic strength. The electrolyte mixtures used and the general compositions are given in the Introduction. Equilibration consisted of rocking the partially filled bottles in the isothermal water bath for 18–22 hr, in general, but occasionally for 3–5 days to confirm the solubility results at the shorter equilibration time. Porous glass filter sticks were then used to procure samples of each saturated solution. One portion of each sample was titrated potentiometrically with standard EDTA (disodium ethylenediamine tetraacetate) solution for total calcium content. A second portion of the sample was used to determine both the density and the total weight of solids per ml for converting molarity to molality and also for verifying the initial dilution of standard solutions. The weight of solids per ml of solution was obtained by evaporating this small known volume of sample to dryness at about 95°C and heating for 16 hr between 190–200°C to dehydrate completely all solids.

RESULTS AND GENERAL DISCUSSION

The average value of 19 determinations over a two-year period for the solubility of $CaSO_4 \cdot 2H_2O$ in water at 25°C is 0.01523 ± 0.00016*m* (average deviation). Equilibration times for these experiments varied from 18 to 112 hr—in excellent agreement with the value of 0.0151*m* from Marshall et al. (*3, 4*).

The solubilities of $CaSO_4 \cdot 2H_2O$ at 25°C in various aqueous mixed electrolyte solutions at approximate ionic strengths of 0.5, 2, and 6 are listed in Table I. The solubilities of $CaSO_4 \cdot 2H_2O$ in the system Na_2SO_4–$NaNO_3$–H_2O are those published previously (*10*). Upon plotting the solubilities of $CaSO_4 \cdot 2H_2O$ in NaCl–H_2O solutions at 25°C vs. the molality of NaCl, the results from this present paper show excellent agreement with the average values from an earlier publication (*3*) at $m = 0.4$ and 2 but were about 4% lower at 5.87*m* NaCl. Unusually long equilibration times (4–5 days) at 6*m* NaCl were necessary to avoid reporting an apparent solubility which is higher than the actual solubility of $CaSO_4 \cdot 2H_2O$. This high apparent solubility at lower equilibration times probably was due to the presence initially of very finely divided solid particles of $CaSO_4 \cdot 2H_2O$. No literature values were found for comparison with our solubilities of $CaSO_4 \cdot 2H_2O$ in aqueous lithium chloride, lithium nitrate, or lithium sulfate solutions.

SOLUBILITY AND ASSOCIATION EQUILIBRIA

Since the experimental equilibrium quotients in this study are expressed in molal units, the molality of water is a constant

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value for all solutions. Hence, Equilibria 1 and 3 are not written in terms of the stable solid $CaSO_4 \cdot 2H_2O$ nor is $[H_2O]^2$ included in the equilibrium quotient expressions. See ref. *10* for further discussion. Again (*10*), the postulated solubility equilibria are

$$CaSO_4(s) \overset{Q_u}{\rightleftharpoons} CaSO_4^0(aq) \qquad (1)$$

and

$$CaSO_4^0(aq) \overset{Q_d}{\rightleftharpoons} Ca^{2+}(aq) + SO_4^{2-}(aq) \qquad (2)$$

where the equilibrium quotient Q_u is the molality of the ion pair $CaSO_4^0$ and Q_d is the ionization or dissociation quotient for this neutral molecule. Therefore, the net equilibrium is

$$CaSO_4(s) \overset{Q_{isp}}{\rightleftharpoons} Ca^{2+}(aq) + SO_4^{2-}(aq) \qquad (3)$$

and the ionic solubility product quotient Q_{isp} is equal to Q_dQ_u. It then follows that the total calcium in solution, s, can be expressed by

$$s = [CaSO_4^0] + [Ca^{2+}] \qquad (4)$$

$$= Q_u + Q_{isp}/[SO_4^{2-}] \qquad (5)$$

$$= Q_u + Q_dQ_u/(\text{total sulfate} - Q_u) \qquad (6)$$

where total sulfate is the sum of s and the molality of added Na_2SO_4 or Li_2SO_4.

The assumptions are made that sodium and lithium salts are completely ionized and that $CaSO_4^0$ ion pairs are formed in significant concentrations, but no ion triplets or quadruplets. On this basis the ionic strengths of the solutions are given by

$$I \text{ (molal units)} = m \text{ of 1–1 electrolyte} + \text{three times the molality of alkali metal sulfate} + 4(s - m \text{ of } CaSO_4^0) \qquad (7)$$

Table I. Molal Solubilities of $CaSO_4 \cdot 2H_2O$ at 25°C in Several Aqueous Mixed Electrolyte Systems

$CaSO_4 \cdot 2H_2O$,[a] m	Na_2SO_4, m	$NaNO_3$, m
I[b] = 0.50 ± 0.01		
0.0344	0	0.376
0.0350	0	0.386
0.0302	0.0103	0.376
0.0261	0.0204	0.356
0.0233	0.0305	0.335
0.0210	0.0408	0.324
0.0186	0.0509	0.294
0.0157	0.0712	0.254
0.0135	0.0915	0.192
0.0104	0.163	0
0.0104	0.163	0
I = 2.11 ± 0.05		
0.0638	0	1.92
0.0431	0.0534	1.86
0.0375	0.0745	1.81
0.0312	0.107	1.70
0.0226	0.174	1.48
0.0177	0.255	1.22
0.0137	0.506	0.51
I = 5.97 ± 0.08		
0.0805	0	5.75
0.0651	0.0359	5.76
0.0568	0.0602	5.62
0.0441	0.108	5.56
0.0329	0.179	5.35
0.0240	0.297	4.97
0.0171	0.580	4.05
0.0165	0.576	4.01
0.0161	0.598	4.17

$CaSO_4 \cdot 2H_2O$, m	Na_2SO_4, m	$NaCl$, m
I = 0.49 ± 0.01		
0.0332	0	0.392
0.0283	0.0102	0.372
0.0245	0.0193	0.344
0.0195	0.0403	0.323
0.0148	0.0702	0.251
0.0123	0.0942	0.160
0.0102	0.160	0
I = 2.07 ± 0.02		
0.0530	0	1.90
0.0441	0.0209	1.87
0.0373	0.0419	1.84
0.0279	0.0836	1.75
0.0197	0.154	1.51
0.0153	0.259	1.24
I = 6.01 ± 0.05		
0.0457	0	5.91
0.0461	0	5.84
0.0465	0	5.87
0.0365	0.0229	5.81
0.0366	0.0226	5.74
0.0364	0.0229	5.81
0.0292	0.0458	5.80
0.0291	0.0454	5.77
0.0245	0.0689	5.75
0.0211	0.0902	5.60
0.0165	0.137	5.58
0.0141	0.170	5.43
0.0138	0.172	5.49
0.0104	0.282	5.10
0.0100	0.291	5.26
0.00994	0.337	3.68
0.00843	0.559	4.22

$CaSO_4 \cdot 2H_2O$, m	Li_2SO_4, m	$LiNO_3$, m
I = 0.51 ± 0.01		
0.0337	0	0.393
0.0288	0.0104	0.377
0.0252	0.0208	0.364
0.0199	0.0416	0.328
0.0149	0.0720	0.252
0.0121	0.103	0.174
0.00962	0.173	0
I = 2.18 ± 0.03		
0.0606	0	1.97
0.0402	0.0557	1.93
0.0348	0.0777	1.88
0.0282	0.110	1.75
0.0200	0.186	1.52
0.0155	0.272	1.30
0.0112	0.531	0.530
I = 5.93 ± 0.05		
0.0783	0	5.68
0.0633	0.0356	5.63
0.0631	0.0357	5.64
0.0430	0.106	5.44
0.0315	0.178	5.33
0.0216	0.296	4.96
0.0128	0.578	4.04
0.0127	0.584	4.08

$CaSO_4 \cdot 2H_2O$, m	Li_2SO_4, m	$LiCl$, m
I = 0.56 ± 0.02		
0.0335	0	0.469
0.0286	0.0104	0.446
0.0283	0.0104	0.449
0.0248	0.0208	0.430
0.0194	0.0414	0.385
0.0147	0.0722	0.301
0.0121	0.103	0.202
0.00979	0.170	0
0.00962	0.168	0
I = 2.10 ± 0.01		
0.0448	0	1.96
0.0360	0.0213	1.93
0.0294	0.0426	1.87
0.0214	0.0852	1.78
0.0144	0.170	1.55
0.0109	0.317	1.12
I = 5.94 ± 0.08		
0.0309	0	5.84
0.0260	0.0114	5.70
0.0216	0.0234	5.85
0.0158	0.0469	5.83
0.0102	0.0940	5.70
0.00691	0.165	5.50
0.00535	0.276	5.01
0.00532	0.274	4.97

[a] Saturating solid phase (molalities expressed as $CaSO_4$). [b] I = ionic strength (molal units).

Table II. Equilibrium Quotients at 25°C for $CaSO_4$ in Several Aqueous Mixed Electrolyte Systems

Mixed electrolyte	$I = 0.5$			$I = 2.1$			$I = 6.0$		
	Q_u	Q_{isp}	Q_d	Q_u	Q_{isp}	Q_d	Q_u	Q_{isp}	Q_d
	$\times 10^{-3}$	$\times 10^{-3}$		$\times 10^{-3}$	$\times 10^{-3}$		$\times 10^{-3}$	$\times 10^{-3}$	
Na_2SO_4–$NaNO_3$	5.08	0.880	0.173	6.07	3.32	0.547	7.28	5.38	0.739
Na_2SO_4–$NaCl$	5.14	0.774	0.150	7.42	2.10	0.283	4.73	1.72	0.363
Li_2SO_4–$LiNO_3$	4.81	0.834	0.174	4.91	3.14	0.639	3.43	5.68	1.65
Li_2SO_4–$LiCl$	4.99	0.802	0.161	6.20	1.51	0.243	2.23	0.827	0.371

A method of nonlinear least squares was used to fit the experimental data to Equation 5 or 6 from which the parameters Q_u and Q_{isp} were calculated by using each set of data. The validity of this approach is shown in Figures 1-4 where plots of the experimental values of solubility vs. $1/[SO_4^{2-}]$ at each constant ionic strength fit well the rectilinear relationship expected from Equation 5. In Table II are compiled the calculated values for Q_u (the intercept), Q_{isp} (the slope), and Q_d for each set of measurements.

The implication of a given straight line in Figures 1-4 is that invariant or nearly invariant activity coefficients exist for Ca^{2+}, SO_4^{2-}, and $CaSO_4^0$ as the electrolyte composition of the solution changes at constant ionic strength. Furthermore, a given line describes the changing solubility of $CaSO_4 \cdot 2H_2O$ in a mixed electrolyte solution at constant ionic strength as the compositions of electrolyte vary from the 1-1 electrolyte on the right, through alkali metal sulfate plus 1-1 electrolyte, to alkali metal sulfate on the left. From the data in Table I the ratio, *R*, of the molality of added sulfate to the molality of the 1-1 electrolyte varies from 0 to infinity in solutions whose ionic strength is 0.5. Therefore, the entire range of compositions between solutions of 1-1 electrolyte only and of alkali sulfate only is covered. However, this ratio varies at the most from 0 to 1 in solutions of $I = 2$ and from 0 to 0.14 at $I = 6$. The limited ranges of *R* at the higher ionic strengths result from the fact that at higher values of *R* the molalities of SO_4^{2-} ion suppress the solubilities of $CaSO_4 \cdot 2H_2O$ to such an extent that the analytical determination for total calcium becomes too imprecise.

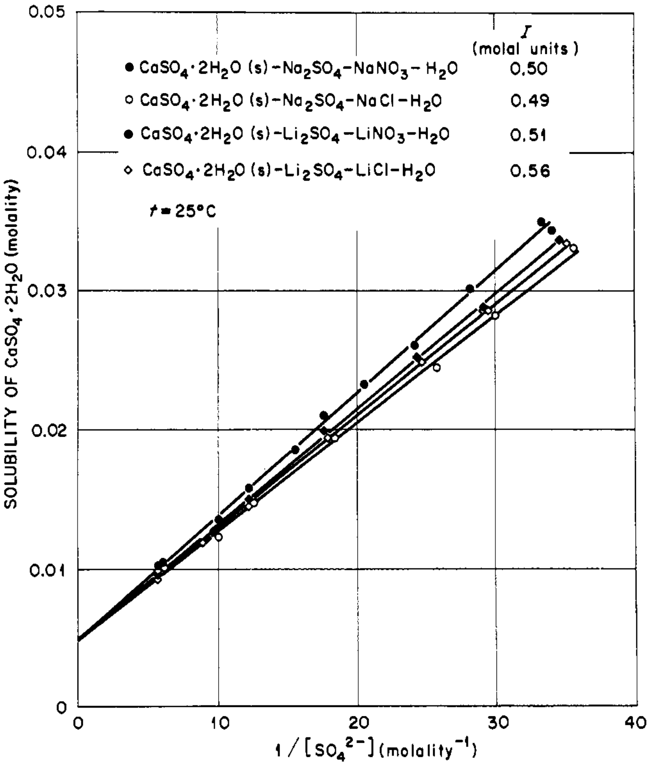

Figure 1. Solubility of $CaSO_4 \cdot 2H_2O$ in mixed electrolytes at 25°C and ionic strength, *I*, of 0.5

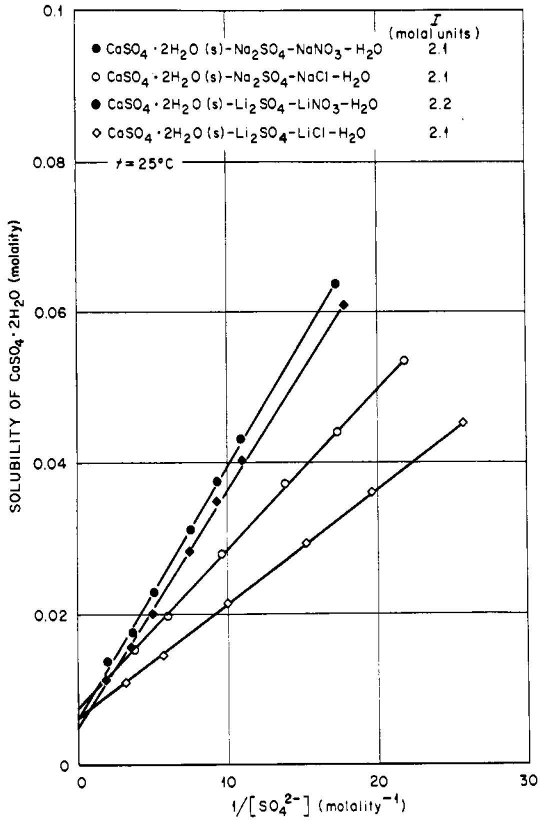

Figure 2. Solubility of $CaSO_4 \cdot 2H_2O$ in mixed electrolytes at 25°C and ionic strength, *I*, of 2

Figure 1 also reveals graphically the fact that the solubility of $CaSO_4 \cdot 2H_2O$ at 25°C and $I = 0.5$ is nearly independent of the source of added sulfate and the supporting electrolyte. Here, Q_u (av) $= 5.01 \times 10^{-3} \pm 2.0\%$, Q_{isp} (av) $= 8.57 \times 10^{-4} \pm 2.7\%$, and Q_d (av) $= 0.168 \pm 5.4\%$ for the four mixed electrolyte systems. Figures 2 and 3, however, show how strongly the solubility of $CaSO_4 \cdot 2H_2O$ can depend upon the chemical nature of the 1-1 electrolyte at constant SO_4^{2-} molality and constant ionic strength for $I = 2$ and 6. The solubilities of the dihydrate are essentially the same for the two nitrate systems at constant ionic strength and SO_4^{2-} molality, but much greater in the presence of nitrate than of chloride. Comparison of the solubility curves again at constant ionic strength and SO_4^{2-} molality for the two nitrate systems suggests that it is unimportant whether the cation is Na^+ or Li^+; on the other hand, the curves for the chloride systems at the higher ionic strengths contradict this observation by showing much greater solubilities of $CaSO_4 \cdot 2H_2O$ in NaCl than in LiCl solutions.

Figure 4 depicts clearly the effect of ionic strength upon solubility at constant SO_4^{2-} molality both within a given mixed electrolyte system as well as among all four systems. In the nitrate systems the solubility of $CaSO_4 \cdot 2H_2O$ increases with an increase

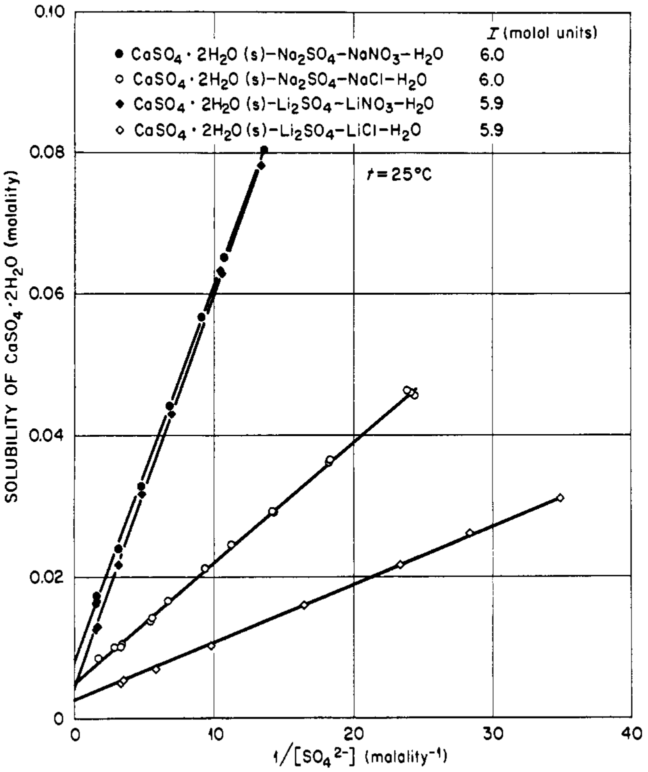

Figure 3. Solubility of $CaSO_4 \cdot 2H_2O$ in mixed electrolytes at 25°C and ionic strength, I, of 6

in ionic strength of the solution to 6. The data of ref. *10* show this to be a monotonic relationship in the $NaNO_3$ system; however, since no $LiNO_3$ systems with an ionic strength between 2 and 6 have been studied, it is possible that the solubility curve passes through a shallow maximum in this range of ionic strengths. Certainly, it is apparent that the solubility of $CaSO_4 \cdot 2H_2O$ in each chloride system reaches a maximum between I = 0.5 and 6. The data of Marshall and Slusher (*3*) reveal that this maximum solubility in the NaCl system occurs at a NaCl molality of approximately 3.4. It is especially startling to find that for the solutions containing LiCl the solubility of $CaSO_4 \cdot 2H_2O$ is actually less at I = 5.9 than at I = 0.56 for the same SO_4^{2-} molality.

In general, both Q_u (the molality of $CaSO_4^0$) and Q_{isp} follow the same relationship to ionic strength as does the solubility. The dissociation quotient, Q_d, increases as ionic strength increases in all four systems, however. The fraction of dissolved calcium sulfate as ion pairs, equal to Q_u/s, decreases from about 15% at the lowest ionic strength for all four systems to as low as 5% at I = 6.

The implausibility of forming additional ion pairs such as $CaNO_3^+$, $CaCl^+$, $NaSO_4^-$, and $LiSO_4^-$ has been discussed in ref. *10;* hence, the arguments will not be repeated here.

AN APPARENT ANOMALY

The discussion above appears to describe adequately the solubility of $CaSO_4 \cdot 2H_2O$ in any one of the four mixed electrolyte systems at a given ionic strength and over the range of compositions studied. The relationship which exists between solubility and the various ionic strengths within a given mixed electrolyte system could be determined presumably by the principles used previously for the system $CaSO_4$–Na_2SO_4–$NaNO_3$–H_2O (*10*). However, none of the above discussion correlates or unifies the solubility results from all four mixed electrolyte systems. For example, the separate systems $CaSO_4 \cdot 2H_2O$(s)–Na_2SO_4–$NaNO_3$–H_2O and $CaSO_4 \cdot 2H_2O$(s)–Na_2SO_4–NaCl–H_2O *must* have the same solubility for $CaSO_4 \cdot 2H_2O$ and the same values for Q_{isp} and Q_u, at constant ionic strength but zero molality of $NaNO_3$ and NaCl, since the two systems reduce to one at this limit—i.e., $CaSO_4 \cdot 2H_2O$(s)–Na_2SO_4–H_2O. Yet the data in Tables I and II and the straight lines in Figure 1 for the two systems at I = 0.5 show different solubilities of $CaSO_4 \cdot 2H_2O$ as well as different values for both Q_u and Q_{isp} at the limit of zero molal for the 1–1 electrolytes, although it is one and the same system.

Unfortunately, at ionic strengths of about 2 and 6 the composition range expressed by R is limited (see above) so that it was not possible *experimentally* for these two four-component systems to become the same three-component system at zero molality of the 1–1 electrolyte. Nevertheless, the curves in Figures 2 and 3 show that at no point do these two systems have the same values for Q_{isp} and Q_u, as they should when they become the same three component system.

The rationale immediately above applies also to the two systems $CaSO_4 \cdot 2H_2O$(s)–Li_2SO_4–$LiNO_3$–H_2O and $CaSO_4 \cdot 2H_2O$(s)–Li_2SO_4–LiCl–H_2O.

CORRELATIVE PROPOSALS

Ionic Strength Considerations. Critical examination of Figures 1–3 reveals that the order of decreasing solubility for $CaSO_4 \cdot 2H_2O$ at a constant molality of SO_4^{2-} is in $NaNO_3$, $LiNO_3$, NaCl, and LiCl solutions. Upon retaining the assumption adopted earlier that all the salts in solution are completely ionized with the exception of $CaSO_4^0$, these differences in solubility might be caused only by the difference in the chemical composition of the alkali metal salts. On this basis, the relative solubilities in $NaNO_3$ and $LiNO_3$ should be approximately the same as the relative solubilities in NaCl and LiCl, since each pair has a common anion and the same cations present. The same behavior then would be expected upon comparing the relative solubilities in $NaNO_3$ and NaCl with the relative solubilities in $LiNO_3$ and LiCl. That this relationship fails to exist is certainly apparent at the two higher ionic strengths.

Therefore, the validity of the assumption regarding complete

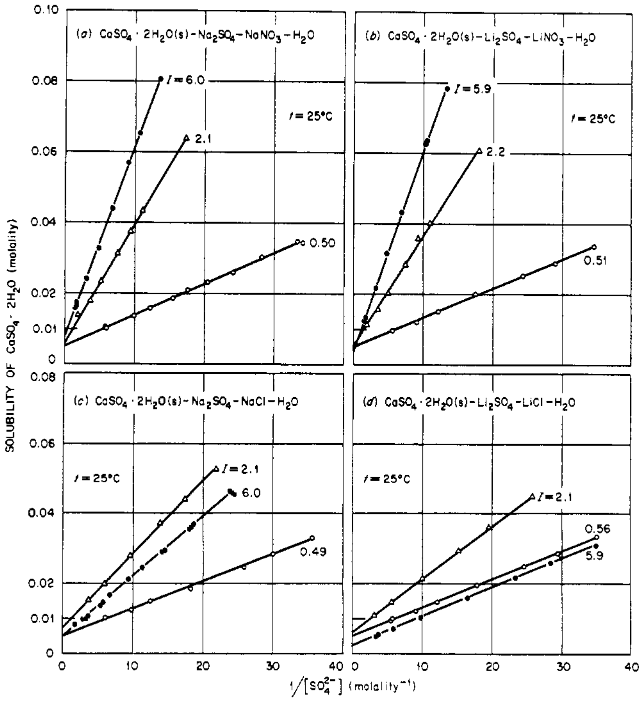

Figure 4. Solubility of $CaSO_4 \cdot 2H_2O$ at 25°C in mixed electrolytes as functions of $1/[SO_4^{2-}]$ and ionic strength, I

ionization of the 1–1 electrolytes at high ionic strengths may logically be questioned. Possibly, the relative differences in solubility discussed above are due mainly to differences in actual ionic strength of the solutions. In other words, association or ion-pair formation may exist to a different degree in the various 1–1 salt solutions; hence, the actual ionic strength of a $NaNO_3$ solution would not be the same as the actual ionic strength of a NaCl solution, although both solutions have the same formal ionic strength. If the assumption is made that the solubility of $CaSO_4 \cdot 2H_2O$ increases monotonically with increasing ionic strength at constant temperature, independent of the 1–1 salt composition, then the order of decreasing ionic association among the 1–1 salt solutions would be LiCl, NaCl, $LiNO_3 \cong NaNO_3$.

It must be emphasized that the conjecture of significant ion-pair formation is considered at this time only at the higher formal ionic strengths. The bases for this consideration in general are the association constants reported for NaCl in water at 25°C to concentrations as high as 1*N* (*1*, *2*, *5*) as well as the association constant estimated from the complete constant approach (*11*). This conjecture may appear at first glance to be contradictory to the earlier statement that insignificant concentrations of the 2–1 and 1–2 ion pairs—i.e., $CaNO_3^+$, $CaCl^+$, $NaSO_4^-$, and $LiSO_4^-$—are formed. However, the maximum formal molalities of Ca^{2+} and SO_4^{2-} are not greater than 0.08, whereas *both* the cationic and anionic species of the 1–1 supporting electrolyte approach formal molalities 80 times greater than this, to approximately 6*m*. Therefore, a considerably smaller association constant for NaCl than for $CaCl^+$ or $NaSO_4^-$ would permit the formation of appreciable concentrations of solvated $NaCl^0$ ion pairs. Similar reasoning may be applied to the other 1–1 salts and their corresponding complexes with Ca^{2+} and SO_4^{2-}.

Solubility Related to "Free" Water. Calculation of the amount of "free" or unsolvated water present in a given solution is another approach which was taken to correlate the solubilities of $CaSO_4 \cdot 2H_2O$ in the various 1–1 electrolyte solutions only—i.e., no alkali sulfate was added. Here the assumption is made that only the "free" water will act as solvent for the dihydrate. Therefore, the solubility data in Table I, at constant ionic strength and SO_4^{2-} molality, indicate that the order of decreasing "free" water content of the solutions is $NaNO_3$, $LiNO_3$, NaCl, and LiCl.

Two properties, vapor pressures of the solutions and hydration numbers, *h*, of the 1–1 electrolytes, were considered individually as a means to evaluate the "free" water content of the solutions. If it is expected that the vapor pressure has a direct relationship with the "free" water molality, the solubilities of $CaSO_4 \cdot 2H_2O$ in $LiNO_3$ and in NaCl solutions are out of order (*7c*). Since there appeared to be no correlation of the assumption with vapor pressure, hydration numbers were then considered as a method to calculate "free" water.

From the many sets of hydration numbers that are available, the values of Sugden (*9*) were used for the "free" water calculations since (*a*) his values were about average of those available and (*b*) his study is one of few that includes all four of the above 1–1 electrolytes, thereby lending some internal consistency to these particular values. Since hydration numbers of Li_2SO_4 and Na_2SO_4 do not appear to be available, it is not possible to include a discussion of those systems to which alkali sulfates were added. With Sugden's results for *h*—i.e., 1.8, 4.4., 7.9, and 10.5 for $NaNO_3$, $LiNO_3$, NaCl, and LiCl, respectively, the number of moles of water solvating the solute species were calculated and subtracted from the total molality of water (55.5*m*) to yield the molality of "free" water. For the same molality of the several 1–1 salts at ionic strengths of 2 and 6, the decrease in the molality of "free" water follows the order predicted above. At $I = 0.5$ there is too small a change both in the calculated molalities of "free" water and in the experimental solubilities of $CaSO_4 \cdot 2H_2O$ in the four 1–1 salt solutions to observe this behavior. The solubility ratio, m ($CaSO_4$)/m ("free" water), is relatively constant (average deviation = 2%) at $I = 2$ but varies by as much as a factor of 3 at $I = 6$.

The interpretation of these calculations, however, is complicated by several factors. A correction should be made for the effects of the small differences in ionic strengths among the various salt solutions in the three vicinities of $I = 0.5$, 2, and 6. Approximate corrections to the same ionic strength—i.e., to 0.5, 2, or 6—were made by the use of equations given previously (*10*) for the ionic solubility product quotient, and for Q_u, of $CaSO_4 \cdot 2H_2O$ in $NaNO_3$ solutions; no better agreement was observed. In addition, association of the 1–1 salts at high ionic strengths, as discussed in the previous section, complicates the assumptions.

It must also be assumed that the solvation numbers used are independent of the molality of the 1–1 salt. This assumption may be reasonably valid at low molalities but probably not at high molalities (*7a*). Also, Sugden's values for *h* of 1.8, 4.4, and 7.9 for $NaNO_3$, $LiNO_3$, and NaCl may be too low. A complete constant approach (*6*) yields a value of about 6.4 at 25°C for the *increase* in hydration number upon ionization for many 1–1 salts, but in the limit of zero ionic strength, and therefore the above values for solvation numbers relating only to the two ions, for example, $Na^+ + Cl^-$, would be expected to be greater than 6.4. It would be predicted also that the solubility product quotient is proportional to the concentration (moles per liter; not molality) of "free" water raised to a power corresponding to the increase in number of moles of water of solvation upon dissolution of the solid phase (*6*). The hypothesis of direct proportionality of the molal solubility of $CaSO_4 \cdot 2H_2O$ to the molality of "free" water provides a total solvation number of 4 which must be divided between Ca^{2+} and SO_4^{2-}. This number appears to be too low, and in the evaluation, units of concentration (moles per liter) were not used.

It must, therefore, be concluded that a qualitative decrease in solubilities with a calculated decrease in "free" water molality is observed, based on a given set of solvation numbers. The interpretation, however, is complicated by many factors, including a lack of sufficient data for a resolution at this time.

Modified Harned's Rule Approach. The solubility of calcium sulfate dihydrate in each separate electrolyte system can be described well also by a modified Harned's rule (*7b*) approach

$$\log\, [m_{\mathrm{Ca(total)}} \cdot m_{\mathrm{SO_4(total)}}] = A + Bm_{as} + Dm_{as}^2 \qquad (8)$$

where m_{as} corresponds to the molality of added alkali sulfate at a constant ionic strength and *A* is the value of the *formal* solubility product quotient at $m_{as} = 0$. The rule has been modified both to add a quadratic term, Dm_{as}^2, since the relationship is not a rectilinear one, and to include systems with three electrolytes in solution as well as two. However, three parameters (*A*, *B*, *D*) are necessary to describe fully the experimental results on this basis, compared to two constants (Q_u, Q_{isp}) required for the present approach that assumes an associated species $CaSO_4^0$. Due to a lack of $CaSO_4 \cdot 2H_2O$ solubilities in solutions of various compositions of these *1–1 salts only*, this rule could not be used to correlate the behavior among the several single systems.

CONCLUSIONS

In this paper, the solubility and association behavior of calcium sulfate dihydrate in several aqueous three-component systems at 25°C have been presented and show excellent, systematic behavior when treated separately in the several systems. The attempt to correlate the solubility behavior among the different systems, however, proves difficult to achieve.

It is clear from the discussion above that several factors, some competitive, determine the solubility behavior of calcium sulfate dihydrate in a given electrolyte solution. Even though no attempt was made to list all the factors involved, it is apparent from the few considered that there is insufficient information at present to evaluate the relationship among such quantities as association quotients and the different hydration numbers of the many solute species, including $CaSO_4^0$, Ca^{2+}, and SO_4^{2-}, at the high formal ionic strengths. Therefore, it does not appear to be possible at this time to correlate by mass-action models the solubilities and association behavior in the many different systems of electrolyte solutions, although excellent correlations of this type are obtained within each system; a Harned's rule approach also provides a correlation, but with greater complexity.

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Second and Third Virial Coefficients for System Tetrafluoromethane–Sulfur Hexafluoride

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The Burnett method was employed to study the volumetric behavior of the tetrafluoromethane–sulfur hexafluoride system from −1.5–150°C at pressures up to 27 atm. The data were analyzed by the method of least squares to determine the second and third virial coefficients of the Leiden equation of state. Mixture virial coefficients are presented as functions of composition at each experimental temperature. Also derived are the pure component and interaction second and third virial coefficients. The De Rocco spherical-shell intermolecular potential energy function was used to fit the pure component second virial coefficient data. An extension of this model to the interaction second virial coefficient for two molecules of different sizes is presented and adequately represents the experimental results of this work.

The detailed *P-V-T* studies of many gases and several mixtures which should exhibit nearly angular independence in their molecular interactions have been described in the literature (*4*, *7*, *14*). Few of these studies report mixture third virial coefficients, and fewer still report interaction third virial coefficients (*23*).

The present investigation aimed to determine the mixture second and third virial coefficients and the interaction second and third virial coefficients for a binary mixture of quasi-spherical molecules using the Burnett method (*3*). This method is particularly advantageous for the study of gas mixtures (*16*, *24*) and requires only repetitive measurements of pressure and temperature.

The tetrafluoromethane–sulfur hexafluoride system was chosen for study because the hard shell and spherical symmetry characteristics of both species make this pair of exceptional interest for the theoretical phase of virial coefficient studies. In addition, the fact that the molecular structure of both compounds consists of a central atom surrounded by fluorine atoms may help to provide insight into the central core–peripheral atom relationship in treatments of fluid mixtures, as well as the nature of the fluorine–fluorine interaction in mixtures of fluorocarbons with the hexafluorides of Group Six.

EXPERIMENTAL

The sulfur hexafluoride was supplied by Air Products and Chemicals, Inc. The analytical report received with the sample showed 50 ppm tetrafluoromethane and less than 3 ppm oxygen, 3 ppm argon, 10 ppm nitrogen, and 34 ppm water. Subsequent mass spectrometric analysis showed that the sample had a minimum purity of 99.99% by volume. The tetrafluoromethane sample was donated by E. I. du Pont de Nemours and Co. The impurities of this material were reduced to less than 0.05% by alternate freezing, melting, and distillation in vacuo.

The volumetric behavior of the system was measured at −1.5°, 35°, 50.4°, 75°, 100°, and 150°C at various compositions, including the pure components at each temperature. The pressure range was from 1–27 atm. Pressures above 18 atm were measured with a Ruska Instrument Corp. deadweight pressure gauge. Lower pressures were measured with a Texas Instruments fused quartz Bourdon gauge. The precision of this arrangement ranged from about two parts in 100,000 at the highest pressure to about one part in 10,000 at the lowest pressure measured. In general, it is believed that systematic errors in pressure were less than 0.015% of the pressure.

The temperature level of the system was established by

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