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Solvent Effects on Solubility and Dehydration of Strontium Chloride

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The solubility of SrCl₂ in mixtures of water with methanol, ethanol, 2-propanol, formic acid, acetic acid, and lactic acid at 25, 50, and 70 °C and the extent of dehydration of SrCl₂·6H₂O in the presence of these solvents have been studied. Achumow's equation is applied for the prediction of solubility of the sait in alcohols.

The salting out phenomenon is well-known, where a salt is added to a homogeneous mixture of two solvents to split this homogeneous phase into two partially miscible liquid phases. Likewise, addition of a nonaqueous solvent (water miscible) to a binary aqueous salt solution can considerably change the solubility and the nature of the equilibrating phase. The effect of such solvents can be known quantitatively by examining the phase diagrams of ternary systems, comprising the salt, water, and different water-miscible solvents, at various temperatures. Such diagrams would give the nature of phase transformation, if any, and the data on the extent of dehydration of a salt. The role of organic solvents in the dehydration of hydrated salts has been studied by many workers.¹⁻⁶

The present work was undertaken to study the solubility of strontium chloride in different organic solvents, such as methanol, ethanol, 2-propanol, formic acid, acetic acid, and lactic acid. The same data indicate the extent of dehydration of hydrates of strontium chloride in the presence of these solvents. The relevant available literature and the solubility data pertaining to these systems at different temperatures are reported elsewhere.

Experimental Section

All chemicals used were of analytical reagent grade. Karl Fisher reagent, for determination of water content, was prepared by a procedure described in the literature.⁸

The experimental studies in phase equilibria involve the following operations: (1) maintenance of constant temperature, (2) equilibration of the reaction complex, (3) separation of liquid phase from solid phase for analysis.

The equilibration cells containing reaction mixtures were immersed in a constant-temperature bath.9,10 The bath liquid was ordinary water, and contained in a rectangular vessel (45 cm \times 30 cm \times 30 cm) made of brass sheet. The cells, in which the complex was equilibrated were made of Jena glass interchangeable ground glass joints. The lower part was about 14 cm long and the stopper (male joint) was 6 cm long. The cells were mounted vertically in the middle on a horizontal brass shaft (3 cm diameter) fixed to the center of the rectangular tank so that rotation of shaft will make the cells turn upside down once every revolution of the shaft. The shaft was rotated by means of worm-worm gears and electric motor, at the rate of about 12 rpm. At a time, six such cells were fixed to the shaft

temp.	liquid g/100 g	compn, of water	
°C	solvent	salt	solid phase(s)
25	61	62.3	SrCl, 6H, O
25	132	74.3	SrCl, 6H, O
25	146	78.5	SrCl, 6H, O
25	156	80.7	$SrCl_{2} \cdot 6H_{2}O + SrCl_{2} \cdot 2H_{2}O$
25	179	83.6	SrCl ₂ ·2H ₂ O
25	211	84.6	SrCl, ·2H, O
25	230	86.7	SrCl ₂ ·2H ₂ O
25	263	89.1	$SrCl_2 \cdot 2H_2O$
25	326	97.2	SrCl ₂ ·2H ₂ O
25	415	113.5	SrCl ₂ ·2H ₂ O
25	521	131.2	SrCl ₂ ·2H ₂ O
25	720	173.2	$SrCl_2 \cdot 2H_2O$
50	49	81.6	$SrCl_2 \cdot 6H_2O + SrCl_2 \cdot 2H_2O$
50	65	82.0	SrCl ₂ ·2H ₂ O
50	167	85.9	$SrCl_2 \cdot 2H_2O$
50	220	90.1	$SrCl_2 \cdot 2H_2O$
50	300	100.0	$SrCl_2 \cdot 2H_2O$
50	342	104.0	$SrCl_2 \cdot 2H_2O$
50	433	121.0	SrCl ₂ ·2H ₂ O
50	546	143.0	SrCl ₂ ·2H ₂ O
50	630	167.0	SrCl ₂ ·2H ₂ O
50	655	165.0	SrCl ₂ ·2H ₂ O
50	680	172.3	SrCl ₂ ·2H ₂ O
70	126	87.3	SrCl ₂ ·2H ₂ O
.70	277	103.0	SrCl ₂ ·2H ₂ O
70	374	120.0	SrCl ₂ ·2H ₂ O
70	430	128.0	SrCl ₂ ·2H ₂ O
70	490	142.0	SrCl ₂ ·2H ₂ O
70	508	146.0	$\operatorname{SrCl}_2 \cdot 2\operatorname{H}_2 O + \operatorname{SrCl}_2 \cdot 2\operatorname{H}_2 O$
70	526	147.0	SICI ₂ ·H ₂ O
70	202	153.5	SICI ₂ ·H ₂ O
70	577	136.5	SrCl ₂ ·H ₂ O

Table I. Strontium Chloride-Formic Acid-Water

and these cells served as the paddle for stirring the bath liquid during equilibration. The level of the bath liquid was so adjusted that the cell is completely immersed in the bath liquid. During sampling, when the shaft is not rotating, the stirring of bath liquid was affected by circulating bath liquid by an external pump. The variation of temperature in various parts of the bath liquid was checked by using a Beckmann thermometer and was found to be less than ± 0.05 °C of the control temperature.

For removal of liquid phase in equilibrium with solid phase, a simple jacketed pipet was used. The bath liquid was circulated in the outer jacket of the pipet in order to obviate any difficulty that may be caused by separation of crystals from the saturated solution during removal and transfer of the solution in the sampling bottle. After removal of the sample of liquid phase for analysis, most of the remaining liquid phase in the cell was removed by suction and the wet solid phase was taken for analyses.

temp,		liquid compn, g/100 g of water		
	°C	solvent	salt	solid phase(s)
	25	427	57.3	SrCl ₂ ·6H ₂ O
	25	496	63.7	SrCl ₂ ·6H ₂ O
	25	725	71.3	$SrCl_2 \cdot 6H_2O + SrCl_2 \cdot 2H_2O$
	25	812	60.3	SrCl ₂ ·2H ₂ O
	25	842	60.5	SrCl ₂ ·2H ₂ O
	25	2080	46.7	SrCl ₂ ·2H ₂ O
	25	7460	131.0	SrCl ₂ ·2H ₂ O
	50	85	73.9	$SrCl_2 \cdot 6H_2O + SrCl_2 \cdot 2H_2O$
	50	136	75.6	SrCl ₂ ·2H ₂ O
	50	141	75.1	SrCl ₂ ·2H ₂ O
	50	156	75.5	SrCl ₂ ·2H ₂ O
	50	385	69.0	SrCl ₂ ·2H ₂ O
	50	508	67.5	SrCl ₂ ·2H ₂ O
	50	531	71.2	SrCl ₂ ·2H ₂ O
	50	717	68.10	SrCl ₂ ·2H ₂ O
	50	1365	61.80	SrCl ₂ ·2H ₂ O
	50	2640	68.50	SrCl ₂ ·2H ₂ O
	50	3800	100.00	$SrCl_2 \cdot 2H_2O + SrCl_2 \cdot H_2O$
	50	6070	154.00	SrCl ₂ ·H ₂ O
	50	8170	196.50	SrCl ₂ ·H ₂ O
	70	332	72.70	SrCl ₂ ·2H ₂ O
	70	401	73.60	SrCl ₂ ·2H ₂ O
	70	547	69.80	SrCl ₂ ·2H ₂ O
	70	593	73.00	SrCl ₂ ·2H ₂ O
	70	759	70.00	SrCl ₂ ·2H ₂ O
	70	1540	75.00	SrCl ₂ ·2H ₂ O
	70	1830	70.20	SrCl ₂ ·2H ₂ O
	70	2000	81.00	
	70	2440	95.20	$S_1 C_1^2 C_1 + S_1 C_2 C_2 C_2$
	70			SICI2'H2O
	70			SICI ₂ ·n ₂ O

Table II. Strontium Chloride-Acetic Acid-Water

Table III.	Strontium	Chloride-	Lactic	Acid-Water
		~ · · · · · · · · · · · ·		

tem	temp, $\frac{g/100 \text{ g of water}}{g/100 \text{ g of water}}$		compn, of water	
°C	2	solvent	salt	solid phase(s)
25	5	225	98.70	SrCl ₂ ·6H ₂ O
25	5	266	109.0	SrCl ₂ ·6H ₂ O
25	5	268	111.0	SrCl ₂ ·6H ₂ O
25	5	301	118.6	SrCl ₂ ·6H ₂ O
25	5	320	124.0	$SrCl_2 \cdot 6H_2O + SrCl_2 \cdot 2H_2O$
25	5	363	139.6	SrCl ₂ ·2H ₂ O
25	5	368	137.5	SrCl ₂ ·2H ₂ O
25	5	473	168.0	SrCl ₂ ·2H ₂ O
50)	84	92.2	SrCl, ·6H, O
50	0	98	96.7	SrCl, 6H, O
50	2	97	95.0	SrCl, 6H, O
50)	111	98.1	$SrCl_{2}.6H_{2}O + SrCl_{2}.2H_{2}O$
50	2	194	114.0	SrCl, 2H, O
50)	308	141.0	SrCl, 2H, O
50)	520	186.0	SrCl, 2H, O
50)	671	220.0	SrCl, 2H, O
70)	176	116.0	SrCl, 2H, O
70)	186	115.0	Sr·Cl.·2H.O
70)	212	121.0	Sr·Cl,·2H,O
70)	263	134.2	SrCl, 2H, O
70)	314	146.0	STCl, 2H, O
70	0	382	160.0	SrCl, 2H, O
70)	802	276.0	SrCl ₂ ·2H ₂ O

The solubility data obtained at different temperatures, with formic acid, acetic acid, and lactic acid are tabulated in Tables I–III and graphically plotted in Figure 1. These data can be plotted on a triangular diagram also, but due to crowding of various points, these are plotted on an enlarged scale on rectangular coordinates. Similar data for methanol, ethanol, and 2-propanol are given in Tables IV–VI and plotted in Figure 2. The points t with subscripts 1 and 2 on the curves in Figures 1 and 2, are transition points with respect to $SrCl_2 \cdot 6H_2O \rightarrow SrCl_2 \cdot 2H_2O$ and $SrCl_2 \cdot 2H_2O \rightarrow SrCl_2 \cdot H_2O$. In terms of phase rule, these points are invariant points, meaning zero degree of



Figure 1. Solubility curves for the system strontium chloride-acid-water.

Table IV. Strontium Chloride-Methanol-Water

temp	liquid compn, g/100 g of water		
°C	solvent	salt	solid phase(s)
25	108	86.2	SrCl, ·6H, O
25	122	92.5	SrCl, 6H, O
25	149	98.5	SrCl, 6H, O
25	148	95.3	$SrC1, \cdot 6H, O + SrC1, \cdot 2H, O$
25	241	116.0	SrCl, 2H, O
25	310	128.0	SrCl, 2H, O
25	385	141.4	SrC1,·2H,O
50	30	76.0	$SrCl_{,} \cdot 6H_{,}O + SrCl_{,} \cdot 2H_{,}O$
50	168	125.0	SrCl, 2H, O
50	284	140.0	SrCl, 2H, O
50	388	157.0	SrCl, 2H, O
50	480	168.0	SrCl ₂ ·2H ₂ O

Table V. Strontium Chloride-Ethanol-Water

tem	liquid $g/100 g$	comp n , of water	
°C	solvent	salt	solid phase(s)
25	327	47.0	SrCl ₂ ·6H ₂ O
25	485	42.2	SrCl ₂ ·6H ₂ O
25	616	36.0	$SrCl_2 \cdot 6H_2O + SrCl_2 \cdot 2H_2O$
25	783	38.4	SrCl ₂ ·2H ₂ O
25	996	35.8	SrCl ₂ ·2H ₂ O
50	70	74.0	$SrCl_{2} \cdot 6H_{2}O + SrCl_{2} \cdot 2H_{2}O$
50	288	59.0	SrCl, ·2H, O
50	320	58.4	SrCl, ·2H, O
50	402	51.7	SrCl, ·2H, O
50	702	48.1	SrCl ₂ ·2H ₂ O

Table VI. Shokhum Chlonde-Flopanol-Wate	Table VI.	Strontium Chloride-Propanol-	Water
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temp.	liquid compn, g/100 g of water				
°C	solvent	salt	solid phase(s)		
25	469	14.0	SrCl ₂ ·6H ₂ O		
25	823	7.1	SrCl ₂ ·6H ₂ O		
25	962	5.4	SrCl ₂ ·6H ₂ O		
25	1572	2.7	$SrCl_2 \cdot 6H_2O + SrCl_2 \cdot 2H_2O$		
25	4660	0	SrCl ₂ ·2H ₂ O		
50	983	12.8	SrCl, ·6H, O		
50	1208	12.5	$SrCl_2 \cdot 6H_2O + SrCl_2 \cdot 2H_2O$		
50	2416	2.5	SrCl ₂ ·2H ₂ O		

freedom. t₁ and t₂ represent the composition of solutions which are saturated with respect to two solid phases; viz., at t₁, phases in equilibrium are saturated solution + SrCl₂·6H₂ + SrCl₂·2H₂O

Table VII. Experimental Results Obtained for the Dehydration of Salts at Different Conditions

	transition liquid compn, g/100 g of solution					
no.	medium	temp, °C	solvent	salt	water	phase reaction
1	air	63				$SrCl_2 \cdot 6H_2O \rightarrow SrCl_2 \cdot 2H_2O + 4H_2O$
2	water	61.4		46.58	53.42	$SrCl_2 \cdot 6H_2O \rightarrow SrCl_2 \cdot 2H_2O + 4H_2O$
3	formic acid + water	25	46.30	24.00	29.70	$SrCl_2 \cdot 6H_2O \rightarrow SrCl_2 \cdot 2H_2O + 4H_2O$
4	acetic acid + water	25	78.50	8.95	12.55	$SrCl_2 \cdot 6H_2O \rightarrow SrCl_2 \cdot 2H_2O + 4H_2O$
5	lactic acid + water	25	58.80	22.80	18.40	$SrCl_2 \cdot 6H_2O \rightarrow SrCl_2 \cdot 2H_2O + 4H_2O$
6	methanol + water	25	43.16	27.74	29.10	$SrCl_2 \cdot 6H_2O \rightarrow SrCl_2 \cdot 2H_2O + 4H_2O$
7	ethanol + water	25	81.88	4.82	13.30	$SrCl_2 \cdot 6H_2O \rightarrow SrCl_2 \cdot 2H_2O + 4H_2O$
8	2-propanol + water	25	93.87	0.16	5.97	$SrCl_2 \cdot 6H_2O \rightarrow SrCl_2 \cdot 2H_2O + H_2O$
9	formic acid + water	50	21.25	35.40	43.35	$SrCl_2 \cdot 6H_2O \rightarrow SrCl_2 \cdot 2H_2O + 4H_2O$
10	acetic acid + water	50	32.80	28.55	38.65	$SrCl_2 \cdot 6H_2O \rightarrow SrCl_2 \cdot 2H_2O + 4H_2O$
11	lactic acid + water	50	36.03	31.70	32.27	$SrCl_2 \cdot 6H_2O \rightarrow SrCl_2 \cdot 2H_2O + 4H_2O$
12	methanol + water	50	14.56	36.91	48.51	$SrCl_{2} \cdot 6H_{2}O \rightarrow SrCl_{2} \cdot 2H_{2}O + 4H_{2}O$
13	ethanol + water	50	29.15	29.50	41.35	$SrCl_{2} \cdot 6H_{2}O \rightarrow SrCl_{2} \cdot 2H_{2}O + 4H_{2}O$
14	2-propanol + water	50	91.48	0.95	7.57	$SrCl_2 \cdot 6H_2O \rightarrow SrCl_2 \cdot 2H_2O + 4H_2O$
15	air	105				$SrCl_2 \cdot 2H_2O \rightarrow SrCl_2 \cdot H_2O + H_2O$
16	water	134.4		56.1	43.9	$SrCl_2 \cdot 2H_2O \rightarrow SrCl_2 \cdot H_2O + H_2O$
17	acetic acid + water	50	95.00	2.50	2.50	$SrCl_{2} \cdot 2H_{2}O \rightarrow SrCl_{2} \cdot H_{2}O + H_{2}O$
18	formic acid + water	70	67.40	19.34	13.26	$SrCl_{2} \cdot 2H_{2} \rightarrow SrCl_{2} \cdot H_{2}O + H_{2}O$
19	acetic acid + water	70	92.60	3.61	3.79	$SrCl_2 \cdot 2H_2O \rightarrow SrCl_2 \cdot H_2O + H_2O$



Figure 2. Solubility curves for the system strontium chloride-alcohol-water.

and at t_2 phases are solution + SrCl₂·2H₂O + SrCl₂·H₂O.

The solubility data obtained at different temperatures, with formic acid, acetic acid, and lactic acid are represented in Figure 1 and data with methanol, ethanol, and 2-propanol are represented in Figure 2. The points t with subscripts 1 and 2 on the curves represent the liquid-phase composition, at which phase transformation takes place. Figure 1 shows that the solubility of strontium chloride increases with increase in the solvent-water ratio in cases of formic and lactic acid. In the case of acetic acid, the solubility of the salt increases slowly until the concentration of the solution reaches the liquid composition at which the phase transformation $SrCl_2 \cdot 6H_2O \rightarrow$ SrCl₂·2H₂O takes place, and beyond this point the solubility decreases slightly and remains steady from the solvent/water ratio of 8 onward. On comparison of the effect of different acids under similar conditions of temperature and solvent/water ratio, the solubility of strontium chloride increases in the order CH₃COOH, HCOOH, CH₃CHOHCOOH solutions. This observation is comparable with the solubility of barium chloride in these three acids.

Figure 2 shows the effect of methanol, ethanol, and 2propanol on the solubility of strontium chloride at 25, 50, and 70 °C. It can be seen from these isotherms that the solubility of strontium chloride increases with increase in the methanol/water ratio, whereas in the case of ethanol and 2-propanol, the solubility decreases. The decrease in the solubility of salt at 25 °C is more sharp in the case of 2-propanol than in ethanol. The solubility data at 50 °C with 2-propanol were collected beyond the solvent/water ratio of 9.8, because at lower ratios two immiscible liquid phases are formed. On comparing the effect of different alcohols under similar conditions of temperature and solvent/water ratio, we found the solubility of strontium chloride increases in the order 2-propanol, ethanol, and methanol. This may be explained by the fact that methanol is the most waterlike substance (hydrogen bonded, high dielectric constant solvent). Methanol maintains much of the nice balance of basic and acidic properties found in water. It has also been reported that aqueous methanol forms a complex in liquid phase of type 3 CH₃OH-7H₂O and that may have an additive effect in enhancing the solubility of the salt. Whereas in the other two alcohols, the low solubility of the salt is due to the absence of hydrogen bonding and low dielectric constant.

On comparing the solubility of the salt between these two groups of solvents, i.e., acids and alcohols, we find it difficult to explain quantitatively the effects of different solvents on the solubility, simply on the basis of values of dielectric constant of individual solvents or solvent–water mixtures. But qualitatively, one can say that protic solvents with higher dielectric constants are better solvents than those having lower dielectric constants. It can be seen that the solubility of strontium chloride under a given set of conditions decreases in the order methanol, lactic acid, formic acid, acetic acid, ethanol, and 2-propanol. The first three solvents are classified as protic solvents with higher dielectric constants. Incidently, with these three solvents, the solution process is also endothermic; l.e., solubility of the salt increases with temperature.

Effect on Phase Transformation or Dehydration of Salts

For comparison, the dehydration temperature obtained by differential thermal analysis and phase transformation temperatures obtained in water and aqueous organic solvent medium are tabulated in Table VII. DTA and TGA analyses showed that phase transformation during dehydration of SrCl₂•6H₂O to anhydrous SrCl₂ takes place as follows:

whereas, in the presence of water, i.e., in the SrCl₂·H₂O binary system, the corresponding phase transformation temperatures are 61.4, 134.4, and 320 °C, respectively. The present work showed that SrCl₂·6H₂O can be partially dehydrated to Sr-





Cl₂·2H₂O even at 25 °C, in the presence of all six solvents under consideration. Further, dehydration from SrCl+2H₂O -SrCl₂·H₂O takes place at 70 °C, in the presence of both formic acid and acetic acid. In fact with acetic acid, the second step can be achieved even at 50 °C. In some cases at very high concentrations of solvents, solid phase in equilibrium with solutions contained a few moles of solvent. These results show that the drop in phase transition temperatures obtained in the presence of solvents is considerable; i.e., by use of organic solvents, hydrated salts can be partially or completely dehydrated at much lower temperatures compared to those involved in the presence of air or pure aqueous systems.

Correlation of Solubility Data in the Form of Achumow's Equation²

It is difficult to predict solubility of electrolytes in solvents, as the solubility of a salt depends upon many factors, such as, dielectric constant, dissociation constant of the solvent, size and charge of ions, temperature, solvent-solute interaction, etc. In some cases, where a salt is insoluble in pure organic liquids, the solubility of salt in organic liquid-water mixtures can be extrapolated or interpolated at a given temperature to limited degree by Achumow's equation

 $y = y_1(1-x)^n$

or

$$\log y = \log y_1 + n \log (1 - x)$$

where v = solubility of salt in solvent-water mixture (mol of salt/100 mol of solvent mixture), y_1 = solubility of salt in pure water (mol of salt/100 mol of water), and (1 - x) = mole fraction of water in solvent-water mixture.

The value of n in the equation is to be found from a few sets of experimental data and plotting log y against log (1 - x). The slope of this line gives the value of n. The data are plotted in Figure 3. The values of the *n* have been found from the linear portion of the curve. The typical equations from which the solubility data can be predicted are as follows for SrCl₂-2propanol-water.

$$y = 6.35(1 - x)^{2.7}$$
 for 25 °C isotherm (1)

$$y = 8.23(1 - x)^{2.3}$$
 for 50 °C isotherm (2)

Similar equations were obtained for other systems with limitations earlier expressed.

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Pressure–Volume–Temperature Relationships of CH₃COOC₂H₅ and Generalized Tait Equation for Liquids at High Pressures

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Experimental P-V-T data of CH₃COOC₂H₅ have been determined for temperatures from -20 to +40 °C and pressures up to 1500 atm with an accuracy better than 0.13%. The Tait equation parameters were correlated by use of 321 P-V-T data points of ten compounds including CH₃COOC₂H₅. The average deviations are 0.5% in the specific volumes calculated by the Tait equation with the correlated parameters.

P-V-T relationships of liquids at high pressures are often unavailable for desired pressures, temperatures, and compounds

in engineering calculations. Various methods have been studied in predicting liquid volumes at high pressures (1-6, 12-17). However, most of these methods are not always possible to estimate with reasonable accuracy the volumetric properties of liquids.

The Tait equation has had considerable success in describing P-V-T data, but this use has been limited to compounds for which the Tait parameters are available. Hence the development of the correlation of the Tait parameters may be useful in the prediction of P-V-T data for a wide range of liquids. It has been previously shown that an approximately linear relationship exists between the reduced Tait parameter, B_T/P_c , and the