Part I

CHEMICAL ENGINEERING
INORGANIC CHEMISTRY
PHYSICAL CHEMISTRY

A Study of the System $CaCl_2$–$ZnCl_2$–H_2O (NaCl Saturated) at 15° C.

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The system calcium chloride–zinc chloride–water (saturated with sodium chloride) at 15° C. was studied and is presented on a sodium chloride-free basis. Sodium chloride solubility is, in all cases, less than 25 wt. %. At least four solid phases in addition to NaCl are indicated: $CaCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 4H_2O$, $CaCl_2 \cdot ZnCl_2 \cdot XH_2O$ and $ZnCl_2$. Experimental data show that the double salt could be either the tetrahydrate or the pentahydrate. There is some evidence that both hydrates exist. Other recent work on this system indicates that the pentahydrate is the stable phase. If this is true, the possibility of two forms of the pentahydrate is suggested. On the basis of data available in the literature, the anhydrous zinc chloride would appear to be metastable to the sesquihydrate. Density and viscosity data at 25° and 50° C. for the solutions saturated at 15° C. and for several unsaturated solutions are given.

RECENT INTEREST in dense salt solutions as weighting or completion fluids in the oil industry has prompted a study of salt combinations suitable for this purpose. The system $CaCl_2$-$ZnCl_2$-H_2O yields solutions of far greater density than those obtainable with sodium chloride. Available data (5) suggested that this ternary system could be quite complex, but the gross error in the solubility of $CaCl_2 \cdot 6H_2O$ in water at 25° C. casts doubt on the reliability of this work. The temperature chosen for the present study was based on the requirement that these solutions be free of solids at the temperature of use; working temperatures of 15° C. or lower are frequently encountered in off-shore drilling. Commercial calcium chloride, which would be employed in the field, was used in part of the study; because this material invariably contains some sodium chloride, and because the sodium chloride solubility in this system is low, the system as studied was saturated with sodium chloride.

EXPERIMENTAL

Materials. Calcium chloride from various sources, usually Columbia "Calcium Chloride Hi-Test Flake" (96% $CaCl_2$, 2% NaCl), was used for compounding the solutions in this study. The sodium chloride was reagent grade, and either reagent or technical grade (97.5% assay) zinc chloride, was employed. One-third of the experiments were performed using all reagent grade chemicals; in two of these only calcium chloride and zinc chloride were used, to determine the effect of the sodium chloride.

Analyses. Zinc was determined, after removing calcium as the fluoride, by titration with ethylenediaminetetraacetic acid (EDTA) using an Eriochrome Black T indicator. Calcium was determined, after removing the zinc as the sulfide at pH 2.5–3 (using a cellulose filter aid), by oxalate precipitation and permanganate completion. Chloride was determined by a modified Volhard procedure. Sodium was determined gravimetrically by precipitation with magnesium uranyl acetate.

Procedure. Commercial constant temperature baths, controlled to within 0.05° C. of the desired temperature, were employed for equilibration and for density and viscosity measurements.

Predetermined quantities of calcium chloride and zinc chloride (and in most cases sufficient sodium chloride to insure its presence in the solid phase) were added to distilled water in heavy-walled citrate bottles. Solution and equilibration were achieved by tumbling the sealed bottles for at least 18 hours (in some instances for as long as four days) at 15° C. After equilibration, the liquid phase was removed through a medium porosity fritted glass filter by nitrogen pressure filtration. Wet residues and

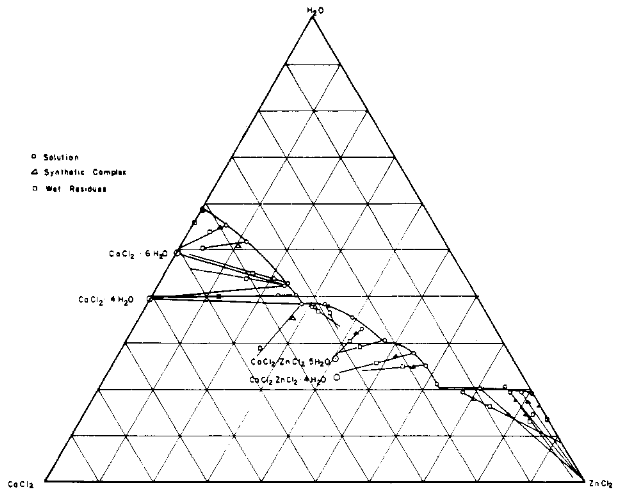

Figure 1. The system: $CaCl_2$–$ZnCl_2$–H_2O (NaCl saturated) at 15.0° C.

filtrates were weighed, and portions were diluted and analyzed for calcium, zinc, chloride and, where appropriate, sodium.

Densities were measured at 25° and 50° C. on portions of the filtrates saturated at 15° C. and on some diluted samples. Density was obtained by determining the volume of a weighed amount of solution in a calibrated Babcock bottle. Viscosities were obtained at 25° and 50° C. on the same solutions used for density determinations. Calibrated Ostwald (Cannon-Fenske modification) pipet viscosimeters were used, and successive readings with the same brine were accepted only when the agreement was within 0.2%.

RESULTS

The experimental data for the system are presented in Table I. Solid phases were estimated by the method of wet residues. While the solutions were saturated with sodium chloride as well as with the indicated solid phases, the data have been calculated on a sodium chloride-free basis for ease of presentation and for the sake of uniformity. However, in the solutions containing less than 40% zinc chloride, the sodium chloride content was less than 1%, and in no case did it exceed 2.5%. The two points in the system determined by use of reagent grade calcium chloride and zinc chloride were not significantly different from adjacent data for solutions containing sodium chloride, nor was there any detectable effect caused by trace impurities in the commerical chemicals.

Figure 1 is a phase diagram for the system showing the 15° C. isotherm, with the lines indicating the wet residues construction from which solid phase compositions were estimated.

The densities and viscosities at 25° and 50° C. of the solutions of various compositions are given in Table II.

DISCUSSION

Considerable difficulty was experienced in defining both the solubility curves and the stable solid phases in the middle portion of the diagram. Contributing to the difficulties were the hygroscopic nature of the solids and solutions, the tendency of the salts to supersaturate, and the high viscosity of the solutions, which hindered the phase separation.

In spite of these difficulties, the data shown in Table I differ in no case from the solution curves of Figure 1 by more than 1% (absolute); in most cases this difference is less than 0.2% (absolute). This holds even if all of the error is assumed to occur in the calcium chloride value. The $CaCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 4H_2O$ solution curves and fields of stability are clearly defined, with the isothermal invariant points bounding these fields established experimentally. The solid phase in the region between 28.5% and 42.1% $ZnCl_2$ is not confirmed. The limited data indicate that a higher hydrate of a $CaCl_2$-$ZnCl_2$ double salt might be stable, although the work of Hudgins (*1*) at 25° C. does not agree with this hypothesis. Stability of $CaCl_2 \cdot ZnCl_2 \cdot 5H_2O$ is clearly indicated between 42.1% and 47.6% $ZnCl_2$,

Table I. Composition Data for the System: $CaCl_2$–$ZnCl_2$–H_2O (NaCl Saturated) at 15° C.

Composition, Wt. %[a]										
Solution				Synthetic Complex			Wet Residue			
$CaCl_2$	$ZnCl_2$	H_2O	NaCl	$CaCl_2$	$ZnCl_2$	H_2O	$GaCl_2$	$ZnCl_2$	H_2O	Solid Phase[b]
41.1	0	58.9	(0.46)	41.2	0	58.8	44.3	0	55.7	$CaCl_2 \cdot 6H_2O$
38.8	6.0	55.2	(0.46)	40.0	5.2	54.8	42.2	3.8	54.0	$CaCl_2 \cdot 6H_2O$
36.9	11.5	51.6	(0.38)	38.9	10.3	50.8	45.3	4.2	50.5	$CaCl_2 \cdot 6H_2O$
33.7	23.6	42.7	(0.31)	35.6	20.6	43.8	38.9	16.1	45.0	$CaCl_2 \cdot 6H_2O$
34.5	23.3	42.2	(0.31)	...	...	...	40.7	15.5	43.8	$CaCl_2 \cdot 6H_2O + CaCl_2 \cdot 4H_2O$
33.2	26.6	40.2	(0.29)	36.7	23.1	40.2	47.8	12.3	39.9	$CaCl_2 \cdot 4H_2O$
33.2	28.5	38.3	(0.29)	36.5	28.2	35.3	45.5	25.2	29.0	$CaCl_2 \cdot 4H_2O$ + 1·1·X
31.6	30.6	37.8	(0.36)	31.0	31.1	37.9	30.9	32.3	36.8	1·1·X
28.9	32.9	38.2	(0.83)	28.5	33.5	38.0	29.0	34.6	36.4	1·1·X
25.1	39.3	35.6	(0.00)	...	...	...	...	...	...	...
24.8	42.1	33.1	(2.02)	26.1	41.6	32.3	28.3	41.1	30.6	1·1·5
21.7	47.6	30.7	(2.13)	22.5	47.2	30.3	27.0	43.7	29.3	1·1·5
17.6	54.5	27.9	(2.45)	21.2	51.6	27.2	25.6	48.6	25.8	1·1·4 or 1·1·5
16.6	58.1	25.3	(1.90)	19.3	55.7	25.0	21.1	53.8	25.1	1·1·4 or 1·1·5
16.8	62.0	21.2	(1.47)	...	...	...	...	...	...	...
12.7	69.9	19.4	(1.59)	11.5	70.4	18.1	9.3	74.4	16.3	$ZnCl_2 \cdot XH_2O$
9.2	70.5	20.3	(1.83)	6.7	78.4	14.9	...	...	...	$ZnCl_2$
4.2	75.0	20.8	(2.11)	3.4	81.7	14.9	...	...	...	$ZnCl_2$
4.0	76.4	19.6	(2.07)	3.9	78.3	17.8	3.5	83.3	13.2	$ZnCl_2$
1.9	78.6	19.5	(2.24)	1.8	80.8	17.4	2.0	83.2	14.8	$ZnCl_2$
0.0	80.8	19.2	(0.00)	0.0	83.2	16.8	0.0	86.4	13.6	$ZnCl_2$

[a] Compositions are calculated on a sodium chloride-free basis except for the sodium chloride itself, which is on an original solution basis and is shown in parenthesis. The sodium chloride contents of the synthetic complexes and wet residue are of no fundamental significance and are not shown.

[b] Solid phases: 1·1·X = $CaCl_2 \cdot ZnCl_2 \cdot XH_2O$; 1·1·5 = $CaCl_2 \cdot ZnCl_2 \cdot 5H_2O$; 1·1·4 = $CaCl_2 \cdot ZnCl_2 \cdot 4H_2O$.

Table II. Densities and Viscosities of Various Calcium Chloride-Zinc Chloride Solutions

Composition, Wt. %[a]			Density, G./Ml.		Viscosity, cp.	
$CaCl_2$	$ZnCl_2$	H_2O	25° C.	50° C.	25° C.	50° C.
27.4	0	72.6	1.252	1.240	2.61	1.66
25.9	4.0	70.1	1.279	1.266	2.60	1.66
24.6	7.6	67.8	1.300	1.286	2.60	1.66
20.7	19.4	59.9	1.395	1.380	2.87	1.83
41.1[b]	0	58.9	1.407	1.391	8.90	4.90
16.8	28.5	54.7	1.439	1.420	3.03	1.89
36.9[b]	11.5	51.6	1.496	1.479	10.8	5.99
38.8[b]	6.0	55.2	1.452	1.436	9.79	5.34
11.9	36.9	51.2	1.503	1.482	3.56	2.14
11.3	41.7	47.0	1.556	1.534	4.38	2.56
8.5	45.8	45.7	1.585	1.562	4.79	2.74
33.7[b]	23.6	42.7	1.605	...	16.7	...
34.5[b]	23.3	42.2	1.609	1.592	18.7	9.68
33.2[b]	26.6	40.2	1.649	...	...	...
28.9[b]	32.9	38.2	1.673	...	...	...
31.6[b]	30.6	37.8	1.679	...	26.8	...
33.2[b]	28.5	38.3	1.682	...	...	...
31.0	29.1	39.9	1.689	1.671	...	...
25.4	38.0	36.6	1.727	...	25.2	...
24.8[b]	42.1	33.1	1.780	1.762	41.0	19.1
21.7[b]	47.6	30.7	1.824	...	...	...
17.6[b]	54.5	27.9	1.913	1.891	88.0	33.5
16.6[b]	58.1	25.3	1.945	...	...	...
7.7	66.2	26.1	1.975	...	...	...
16.8[b]	62.0	21.2	2.028	2.006	326	92.4
12.7[b]	67.9	19.4	2.092	2.069	561	131
1.9[b]	78.6	19.5	2.166	...	...	...
0[b]	80.8	19.2	2.194	...	...	...

[a] Sodium chloride-free basis. [b] Saturated at 15° C.

and it is more likely that this hydrate is stable over the entire range between 28.5% and 47.6% $ZnCl_2$.

At higher zinc chloride levels, the present work indicates that $CaCl_2 \cdot ZnCl_2 \cdot 4H_2O$ is the stable solid phase, although the data could be interpreted as again indicating the pentahydrate. In Hudgins' work at 25° C. the pentahydrate is clearly defined, and it is unlikely that a lower hydrate would exist at a lower temperature in the same region. It should be noted that the pronounced inflection (Figure 1) at 48% $ZnCl_2$ can also be inferred from Hudgins' data at both 0° and 25° C. This suggests regions of stability of two discrete solid phases. Accordingly, the existence of two modifications of $CaCl_2 \cdot ZnCl_2 \cdot 5H_2O$ may be indicated.

The zinc chloride field in Figure 1 is probably metastable; with one exception the experimental tie lines indicate anhydrous zinc chloride to be the solid phase, while literature data *(4)* show the sesquihydrate to be the stable salt in the system $ZnCl_2$–H_2O at 15° C. and the anhydrous salt to be metastable. All the experiments in this portion of the phase diagram were equilibrated for at least two and sometimes four days with no apparent changes. Seeding the solutions with various zinc chloride hydrates during equilibration failed to yield different results.

The densities of the solutions agree well with the previous data of Mead and Fuoss *(2)* for the ternary system $CaCl_2$–$ZnCl_2$–H_2O. If straight lines of constant density are constructed on a triangular composition diagram based on density data for the $CaCl_2$–H_2O *(3)* and $ZnCl_2H_2O$ *(4)* systems, the compositions given in Table II and by Mead and Fuoss would be estimated by interpolation to be an average of 0.003 gram/ml. higher than indicated experimentally. Accordingly, there appears to be a slight bowing of the lines of constant density. The data are insufficient to define this family of curves accurately.

The viscosities of the solutions increase rapidly with increasing salt concentration. If the data of Table II are plotted on the phase diagram (Figure 1), marked curvature in the lines of constant viscosity is shown.

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