Solubility and Density Studies of the $CaCl_2$–$ZnCl_2$–H_2O System at 0° and 25° C.

C. M. HUDGINS
Continental Oil Co., Ponca City, Okla.

The $CaCl_2$–$ZnCl_2$–H_2O system has several advantages for use as a high density fluid in certain operations in the production of oil. The results reported in this paper include density and solubility limits at 0° and 25° C. for various proportions of $ZnCl_2$ and $CaCl_2$ in water. Four solid phases were observed: $CaCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 4H_2O$, $CaCl_2 \cdot ZnCl_2 \cdot 5H_2O$, and $ZnCl_2 \cdot XH_2O$. The double salt pentahydrate has not been previously reported in the literature. Electrical conductivity measurements were also made on the solution phase.

SALT SOLUTIONS are frequently used in oil or gas production to provide hydrostatic pressure (*3*) capable of holding the hydrocarbons in place in the reservoirs. Solutions of NaCl have been used for this purpose for many yeara, and use of $CaCl_2$ began in the 1950's. However, the maximum usable densities of these solutions (1.26 and 1.40 gram/ml.) were still not high enough for many pressure gradients in deep, high pressure wells.

Over a hundred compounds and compound mixtures were considered before it was decided that a solution containing $CaCl_2$ and $ZnCl_2$ offered enough capabilities for use above 1.4 gram/ml. to warrant further study.

A search of the literature revealed that very limited information was available on the $CaCl_2$–$ZnCl_2$–H_2O system. Mead and Fuoss (*4*) reported some solution properties at various temperatures. Tschischifoff and Schachoff (*7*) had obtained some solubility data at 25° and 60° C. However, their data show lower solubilities at 60° than at 25° C. for the middle portion of the curve, which did not seem plausible. Further, the solubility of $CaCl_2$ is in serious disagreement with other data (*4*). A review of the $CaCl_2$–H_2O (*5*) and $ZnCl_2$–H_2O (*6*) systems indicated that the ternary system might be quite complex. Cost considerations and preliminary corrosion testing indicated that the aqueous $CaCl_2$–$ZnCl_2$ system was the best for use at densities between 1.4 and 1.7 gram/ml. It was decided to proceed with a more precise definition of the system.

Composition, density, and solubility relationships were the primary variables under study. Preliminary tests indicated that the salts were more soluble at higher temperatures (at least to 150° C.) and the solubility portion of the problem reduced to a definition of the solubility curves at 0° C. and 25° C. Electrical conductivity data were obtained because of implications concerning the corrosivity of the solutions.

EXPERIMENTAL

The procedure for obtaining saturated solutions was essentially the same for all data points. A preliminary saturation curve was obtained by adding distilled water slowly (days) to various ratios of $CaCl_2$ and $ZnCl_2$ until the solids were almost dissolved. Based on this curve, predetermined amounts of $CaCl_2$, $ZnCl_2$, and distilled H_2O were then placed in containers, sealed, and heated until all solids were dissolved. Baker's Analyzed Reagents were used without further purification. The containers then were placed in a holder on an oscillating shaker and immersed in a constant temperature bath.

Temperature was maintained with a commercially available thermistor controller (±0.1° C.). The 25° C. temperature was checked against an NBS thermometer and the 0° C. bath against a Beckman thermometer calibrated in a triple point cell. Cooling of the 0° C. bath was accomplished with a commercial laboratory refrigerator modified to allow rapid cycling.

Each sample was checked at successive intervals to insure that the ratio of solid to liquid allowed reasonable fluidity with adequate solids. More solids or water was added if necessary, the solution being reheated if solids were added. After all samples were adjusted, the group was agitated vigorously in the constant temperature bath for one week or longer before analyzing.

Liquid samples were removed by filtering through one cm. medium glass frits attached to the end of a glass tube. In the 25° tests supernatant liquid was decanted into the tube and filtered rapidly by the application of 25 p.s.i.g. helium pressure. The filtrate was caught in a weighed 100 ml. volumetric flask. Solid samples were obtained by placing wet solids in a similar fritted glass tube and centrifuging 1–2 minutes. Solids essentially free of mother liquor were obtained in this manner. One portion of the solid was transferred immediately to a weighed 100 ml. volumetric flask for wet chemical analysis, while a second portion was placed in a sealed vial and stored in the constant temperature bath for x-ray studies. The samples in the flasks were diluted to 100 ml. with water containing one ml. concentrated HNO_3 for preventing precipitation of zinc compounds. Wet chemical analyses were subsequently performed on aliquots from these solutions.

Liquid samples were removed from the 0° C. test by inserting a precooled fritted glass tube into the solution. The tube was fitted with a rubber diaphragm top through which was inserted a hypodermic needle attached to a vacuum line. The filtered liquid was poured from the tube into a weighed volumetric flask and treated as before. Solids analysis was not performed in the 0° C. tests.

The wet chemical analysis was performed on aliquots, chloride being determined by the Volhard method and Zn^{++} and Ca^{++} being determined by chelometric titrations. Total calcium and zinc was determined at pH 10 using CDTA (cyclohexanediamine tetraacetic acid, disodium salt) as the chelon and Calmagite [1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid] as the indicator. Calcium was determined separately by masking the zinc with tetraethylene pentamine. Zinc was determined in the presence of calcium at pH 4.5 using dithizone as the indicator. Cation-chloride ion balance discrepancy averaged 1.83 per cent of the value with a standard deviation of 1.61 per cent. Water was determined by difference.

Electrical conductivity measurements were made in a U-type conductance cell, standardized against saturated NaCl, maximum conductivity H_2SO_4 (density 1.223 at

18° C.), and maximum conductivity $MgSO_4$ (density 1.190 at 18° C.) (*6*). The cell constant (measured resistance times specific conductance in reciprocal ohms per cm. of the standard solutions) was 38.4 ± 0.2. A commerical conductivity bridge (Industrial Instruments, Inc., model RC-16B) was used to obtain measurements at 1,000 c.p.s.

Density determinations were performed using either a two ml. or 25 ml. pycnometer or a hydrometer, depending on the quantity of sample available. Measurements were made at ambient temperature and corrected to 15° C. using an average temperature correction of 0.007 gram/ml./10° C. Cross-determinations on identical samples at different temperatures with various density measuring techniques gave results accurate to ±0.005 gram/ml.

An attempt was made to obtain positive structural identification of the solid phases using x-ray diffraction techniques. A General Electric XRD-3 unit was modified to allow samples to be run in an inert atmosphere at a controlled temperature. Samples were placed in an aluminum tray (with and without rapid grinding under a nitrogen blanket) and patterns obtained after various periods of time. Both Cu and Fe targets were used. In spite of the precautions taken, only qualitative results were obtained.

RESULTS

The solubility data are tabulated in Table I and are presented graphically in Figure 1. The isodensity lines on Figure 1 were drawn as best fits for forty points [including data from Hodgman (*2*)] with no deviation

Table I. Solubility of $CaCl_2$–$ZnCl_2$ Mixtures in Water in Weight Per Cent

0° C.		25° C.					
		Solution		Solid Phase			
$CaCl_2$	$ZnCl_2$	$CaCl_2$	$ZnCl_2$	$CaCl_2$	$ZnCl_2$	H_2O	Compound[a]
35.5	0	47.3	0	...	...	...	a
37.4	3.9	43.3	6.0	...	...	...	a
33.3	10.9	38.9	14.3	...	...	...	a
31.0	19.0	41.7	19.4	...	...	...	b[b]
30.6	21.9	41.3	19.1	...	...	...	b[b]
30.0	27.0	36.7	19.6	...	...	...	b
30.0	29.0	33.7	22.4	...	...	...	b
30.0	30.0	35.3	27.5	58.0	3.1	38.9	b + c
30.6	29.8	35.3	26.4	57.2	3.5	39.3	b + c
29.5	30.1	35.3	27.1	58.6	2.5	38.9	b + c
29.5	29.1	35.0	27.5	58.6	2.5	38.9	b + c
28.0	33.0	34.6	28.8	35.2	37.8	27.0	c
20.0	43.0	30.9	31.5	...	...	...	c
20.0	47.0	28.8	34.6	...	...	...	c
18.0	52.0	24.3	45.0	32.7	40.5	26.8	c
17.0	54.0	23.9	47.6	32.7	40.9	26.4	c
0	65.5[c]	22.4	48.9	32.2	41.3	26.5	c
		20.5	53.3	31.6	40.7	27.7	c
		19.9	57.8	31.4	42.8	25.8	c + d
		0	80.0[c]				

[a] a = $CaCl_2 \cdot 6H_2O$, b = $CaCl_2 \cdot 4H_2O$, c = $CaCl_2 \cdot ZnCl_2 \cdot 5H_2O$, d = $ZnCl_2 \cdot XH_2O$. [b] Probably metastable. [c] Ref. 5.

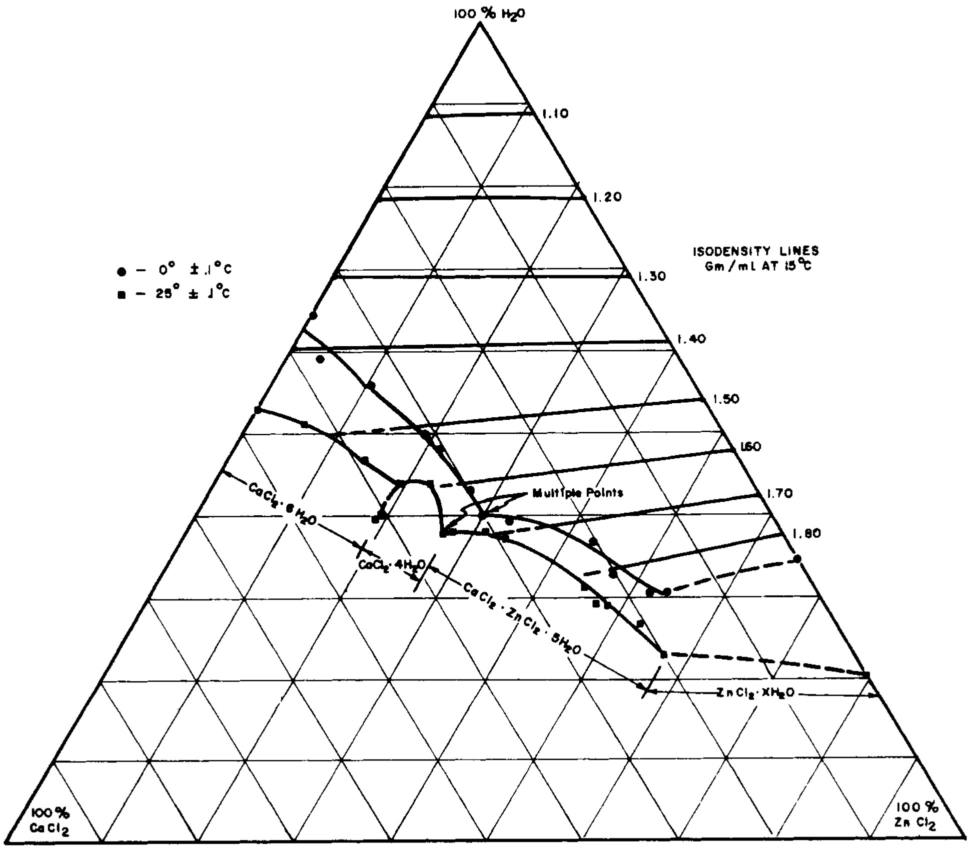

Figure 1. Solubility limits of the $CaCl_2$–$ZnCl_2$–H_2O system at 0° and 25° C. Density curves at 15° C.

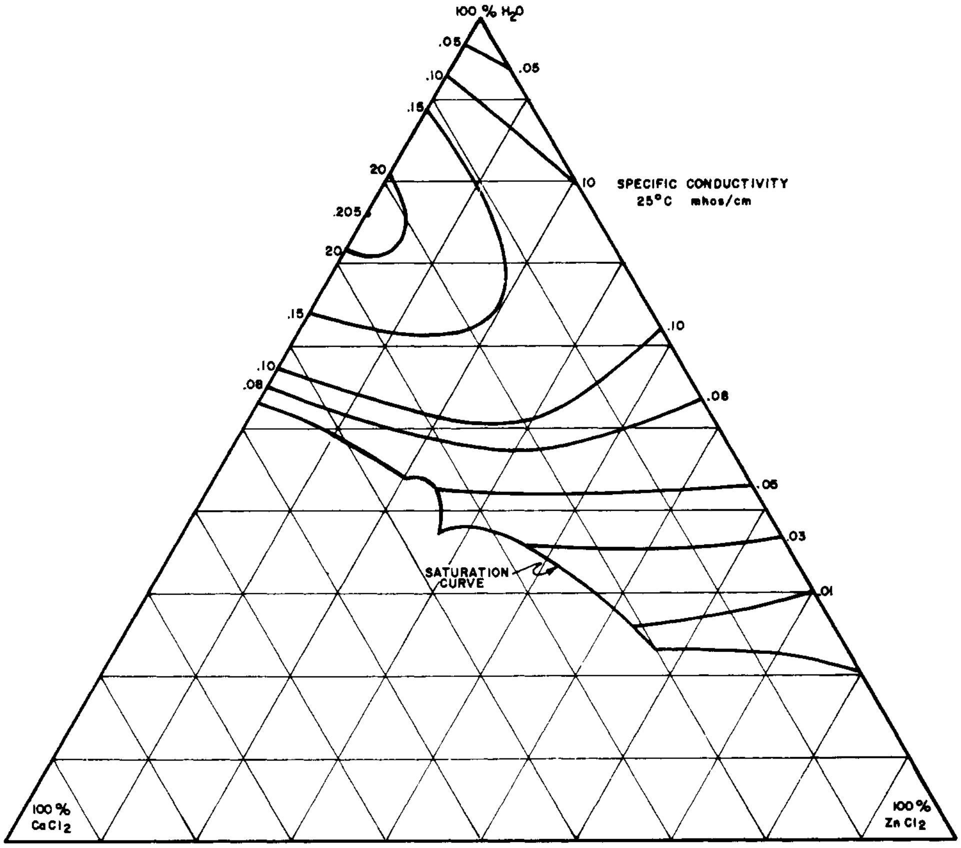

Figure 2. Specific conductivity of $CaCl_2$–$ZnCl_2$–H_2O solutions at 25° C.

greater than 3%. The isoconductivity lines shown in Figure 2 are best fits (±10%) from sixty points including data from Mead and Fuoss (*4*). The x-ray studies essentially confirmed the wet chemical analysis of the solids within the limits discussed below.

DISCUSSION

The presence of four equilibrium compounds is the most obvious feature of Figure 1. No previous record of the existence of $CaCl_2 \cdot ZnCl_2 \cdot 5H_2O$ was found. The $CaCl_2 \cdot 4H_2O$ and $CaCl_2 \cdot ZnCl_2 \cdot 5H_2O$ were adequately defined by the wet analyses shown. The $CaCl_2 \cdot 6H_2O$ and $ZnCl_2 \cdot XH_2O$ were tentatively identified in the preliminary solubility studies by emission spectrographic analysis and reasonably well confirmed by x-ray diffraction analysis in the final studies. The absence of complete x-ray data on the salts and their hydrates hindered precise identification. For example, Bassett and coworkers (*1*) have reported three forms of $CaCl_2 \cdot 4H_2O$, but only one x-ray pattern is in the literature (ASTM 1-1080). This agreed qualitatively with the pattern found for the $CaCl_2 \cdot 4H_2O$ formed in these tests. An x-ray pattern was deduced for the $CaCl_2 \cdot ZnCl_2 \cdot 5H_2O$; however, wide variations in intensities and slight shifts in *d* spacings prevent inclusions of the x-ray data even on a tentative basis. X-ray patterns were adequate to distinguish these normal solubility solids from each other and from the $ZnCl_2 \cdot 4Zn(OH)_2$ (ASTM 7-155) formed as a result of the corrosion of steel samples immersed in the solution during other studies on the system

The effects of the conductivity on the corrosivity of the system were masked by the low pH's and the generally high conductivity. The data have been included for the benefit that others might obtain. The decrease is specific conductivity strikingly points out the reduction in ionization of the salts as their concentration increases to very high levels.

ACKNOWLEDGMENT

This work was part of a larger project in which a number of people were involved: D.F. Hagen and F.H. Meyer, analysis; H.B. Berry and F.D. Koons, experimental; and J.E. Landers and B.L. Carlberg, preliminary testing and planning. The author wishes to thank the management of Continental Oil Co. for permission to publish this paper.

LITERATURE CITED

(1) Bassett, H., Barton, C.W., Foster, A.R., Pateman, C.R.J., *J. Chem. Soc.* **1933**, p. 151.
(2) Handbook of Chemistry and Physics, C.D. Hodgman, ed., 31st ed., 1. 1994, Chemical Rubber Publishing Co., Cleveland, Ohio, 1949.
(3) Hudgins, C.M., Landers, J.E., Greathouse, W.D., *Corrosion* **16**, 535t (1960).
(4) Mead, D.J., Fuoss, R.M., *J. Phys. Chem.* **49**, 480 (1949).
(5) Seidel, A., "Solubilities of Inorganic and Metal Organic Compounds," 3rd. ed., Vol. **I**, Van Nostrand, New York, p. 280 (1940).
(6) *Ibid.*, p. 1582.
(7) Tschischifoff, D.M., Schachoff, A.S., *Zhur. Priklad. Khim.* **9**, 1387 (1936).

RECEIVED for review July 18, 1963. Accepted January 15, 1964.