[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF CASE SCHOOL OF APPLIED SCIENCE]

Equilibria in Saturated Solutions. I. The Ternary Systems $CaCl_2$–$MgCl_2$–H_2O, $CaCl_2$–KCl–H_2O, and $MgCl_2$–KCl–H_2O at 35°

BY WILLIAM J. LIGHTFOOT AND CARL F. PRUTTON

The three isotherms for the systems $CaCl_2$–$MgCl_2$–H_2O, $CaCl_2$–KCl–H_2O and $MgCl_2$–KCl–H_2O, were investigated to supplement the existing data required in problems such as the crystallization and separation processes for brines composed essentially of these salts and water. References to most of the published work on these systems are to be found in Seidell[1] and in the two papers of Igelsrud and Thompson.[2,3]

Experimental Method

A.C.S. reagent grade salts were used in preparing samples for the solubility studies. In the case of the solubilities of the pure salts, recrystallized material was used. The common procedure employed in phase rule studies was followed where mixtures of salts and water were agitated in glass bottles in a thermostat maintained at 35 ± 0.02°. Periodically the solid phases were identified by examination of a drop of the mixture with a petrographic microscope. Each sample was seeded with the appropriate crystal phase. Equilibrium was attained in six to eight hours of stirring as proven by the excellent agreement of results from super- and under-saturation. However, the samples were actually agitated for three to six days before analysis. Pipettes, fitted with small cotton filter plugs, were used to sample the saturated solution. Aliquot portions were taken for analysis.

Total chloride content was determined by titration of an aliquot with silver nitrate using dichlorofluorescein as indicator. In the systems containing calcium, calcium was found by the double precipitation as calcium oxalate followed by titration with standard potassium permanganate. Potassium was determined as the chloroplatinate directly on a separate sample of saturated solution. Magnesium was calculated by difference in all cases, frequently being checked by precipitation with 8-hydroxyquinoline.

TABLE I

THE TERNARY SYSTEM $CaCl_2$–$MgCl_2$–H_2O AT 35°

Saturated solution Weight per cent.		Wet residue Weight per cent.		
$CaCl_2$	$MgCl_2$	$CaCl_2$	$MgCl_2$	Solid phase
51.33	0	...	...	$CaCl_2·4H_2O\alpha$
49.09	2.10	57.99	0.97	$CaCl_2·4H_2O\alpha$
47.75	3.50	54.70	1.96	$CaCl_2·4H_2O\alpha$
45.03	6.20	50.20	9.04	$CaCl_2·4H_2O\alpha$ + Tach.
45.03	6.20	39.25	16.84	$CaCl_2·4H_2O\alpha$ + Tach.
45.07	6.22	38.17	14.99	Tachydrite
39.25	9.49	34.13	17.46	Tachydrite
35.64	11.88	31.69	18.89	Tachydrite
35.15	12.19	29.14	22.64	Tachydrite
30.06	15.67	25.14	26.82	Tachydrite
26.98	17.95	25.43	23.54	Tachydrite
26.78	18.04	24.95	25.02	Tachydrite
26.70	18.13	20.22	27.04	Tach. + $MgCl_2·6H_2O$
26.66	18.24	16.42	30.97	Tach. + $MgCl_2·6H_2O$
23.15	20.28	10.08	35.36	$MgCl_2·6H_2O$
18.89	23.17	8.25	36.50	$MgCl_2·6H_2O$
9.81	29.07	7.38	33.56	$MgCl_2·6H_2O$
3.63	33.56	1.75	40.28	$MgCl_2·6H_2O$
0	36.28	...	...	$MgCl_2·6H_2O$

The solid phases encountered were identified both by graphical plotting of tie-lines according to Schreinemakers' method and by microscopic examination. It was possible to obtain analyses on separate solutions of fixed composition, *e. g.*, solubility of pure salts or isothermally invariant points, that were well within the limits for the experimental methods involved.

The Ternary System $CaCl_2$–$MgCl_2$–H_2O; Table I, Fig. 1.—There are three sections to the solubility curve at this temperature representing solutions in equilibrium with $CaCl_2·4H_2O\alpha$, tachydrite ($CaCl_2·2MgCl_2·12H_2O$) and $MgCl_2·6H_2O$, respectively, the isothermally invariant solutions having the compositions 45.03% $CaCl_2$, 6.20% $MgCl_2$, and 26.68% $CaCl_2$, 18.19% $MgCl_2$. In the 25° isotherm determined by Lee and Egerton[4] tachydrite is just starting to open its field of existence, being formed only at temperatures above 21.95°. At 25 as well as 35°, tachydrite shows incongruent solubility; its area of existence has about doubled in the ten degree rise in temperature

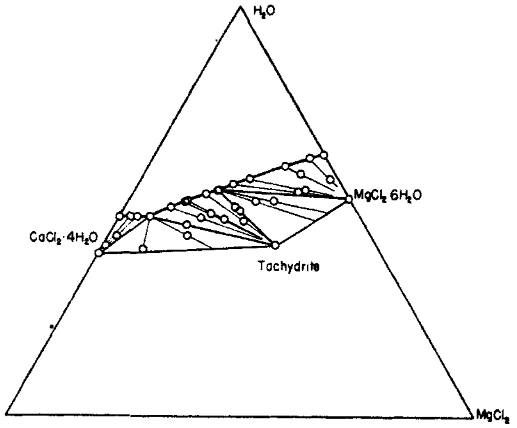

Fig. 1.—The ternary system $CaCl_2$–$MgCl_2$–H_2O at 35°.

The Ternary System $CaCl_2$–KCl–H_2O; Table II, Fig. 2.—This system shows two segments in the solubility curve, one for solutions in equilibrium with potassium chloride, the other for those in equilibrium with $CaCl_2·4H_2O\alpha$. The solution which is in equilibrium with the two solid phases at 35° has the composition 50.45% $CaCl_2$ and 6.48% KCl. No evidence of any binary or ternary compound formation was found. Other investigators working up to 30° have brought forth no ternary compound formation.

If a saturated solution of the isothermally invariant composition, point E Fig. 2, be diluted with water at 35°, solid potassium chloride will start to precipitate out. As more water is added, more potassium chloride will precipitate, reaching a maximum at Y. Continuing with the addition of water, the potassium chloride will dissolve, being in complete solution at X. This type of retrograde solubility has been observed before in solubility studies. The effect in this case is probably more pronounced than that commonly found.

---

[1] Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Vol. I, third ed., Van Nostrand, 1940.

[2] Igelsrud and Thompson, THIS JOURNAL, 58, 318 (1936).

[3] Igelsrud and Thompson, *ibid.*, 58, 2003 (1936).

[4] Lee and Egerton, *J. Chem. Soc.*, 123, 706 (1923).

TABLE II

THE TERNARY SYSTEM $CaCl_2$–KCl–H_2O AT 35°

Saturated solution		Wet residue		
Weight per cent.				
$CaCl_2$	KCl	$CaCl_2$	KCl	Solid phase
0	28.04	...	...	KCl
3.12	24.66	1.70	58.59	KCl
7.28	20.77	2.59	71.71	KCl
13.37	15.59	5.30	66.67	KCl
19.75	10.77	8.60	62.09	KCl
26.45	6.89	13.10	54.08	KCl
31.56	4.89	18.27	44.87	KCl
38.37	3.74	17.78	55.25	KCl
43.56	4.25	24.89	45.36	KCl
46.48	4.90	32.73	32.67	KCl
47.65	5.10	32.66	35.11	KCl
50.47	6.48	44.21	26.51	KCl + $CaCl_2 \cdot 4H_2O\alpha$
50.43	6.48	55.46	7.88	KCl + $CaCl_2 \cdot 4H_2O\alpha$
50.70	3.26	58.10	0.92	$CaCl_2 \cdot 4H_2O\alpha$
51.02	1.28	60.48	.05	$CaCl_2 \cdot 4H_2O\alpha$
51.06	0.82	59.75	.15	$CaCl_2 \cdot 4H_2O\alpha$
51.33	0	...	...	$CaCl_2 \cdot 4H_2O\alpha$

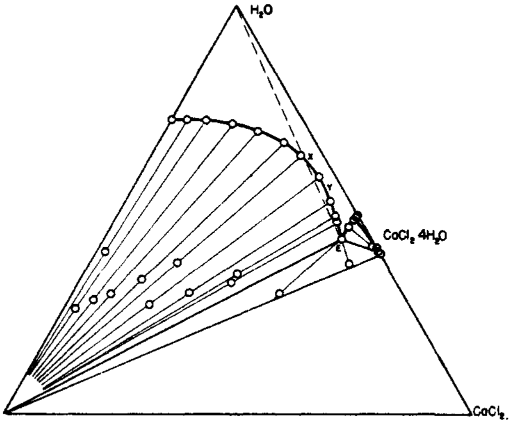

Fig. 2.—The ternary system $CaCl_2$–KCl–H_2O at 35°.

TABLE III

THE TERNARY SYSTEM $MgCl_2$–KCl–H_2O AT 35°

Saturated solution		Wet residue		
Weight per cent.				
$MgCl_2$	KCl	$MgCl_2$	KCl	Solid phase
0	28.04	...	...	KCl
3.70	23.53	1.70	64.91	KCl
9.41	16.95	4.53	59.70	KCl
15.24	11.42	7.38	57.10	KCl
21.41	6.85	9.96	57.09	KCl
27.32	3.80	25.59	24.04	KCl + carnallite
27.34	3.81	28.13	21.74	KCl + carnallite
30.40	1.38	31.30	8.06	Carnallite
33.63	0.38	33.90	17.11	Carnallite
36.17	.14	36.55	10.86	Carn. + $MgCl_2 \cdot 6H_2O$
36.17	.14	39.90	4.89	Carn. + $MgCl_2 \cdot 6H_2O$
36.28	0	...	...	$MgCl_2 \cdot 6H_2O$

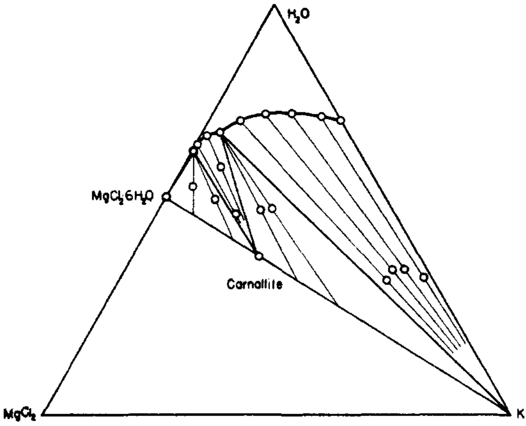

Fig. 3.—The ternary system $MgCl_2$–KCl–H_2O at 35°.

The Ternary System $MgCl_2$–KCl–H_2O; Table III, Fig. 3.—The three sections of the solubility curve represent solutions in equilibrium with $MgCl_2 \cdot 6H_2O$, carnallite, and potassium chloride, and are characterized by the extremely small area of existence of $MgCl_2 \cdot 6H_2O$. This ternary system has been reported at temperatures above and below 35°, and the results at this temperature are in agreement with those reported by others. Most of these workers reported the potassium chloride content by difference in their chemical analyses. Hence, it was not unusual that the potassium chloride content for the isothermally invariant point, where the solid phases are $MgCl_2 \cdot 6H_2O$ and carnallite, should differ slightly, especially since the solution composition is only 0.14% KCl. Values previously reported have been somewhat higher. The solution in equilibrium with potassium chloride and carnallite has the composition 27.33% $MgCl_2$ and 3.81% KCl. Because of the very short curve for $MgCl_2 \cdot 6H_2O$, the phase was identified only by microscopic identification, since graphical determination was not feasible.

The solubilities of the individual salts determined at 35° agree well with the literature data.

The authors wish to thank Dr. R. L. Barrett for his assistance in the interpretation of the crystalline properties of the substances encountered in the experimental portion of the study.

Summary

1. Isotherms have been determined at 35° for the ternary systems $CaCl_2$–$MgCl_2$–H_2O, $CaCl_2$–KCl–H_2O, and $MgCl_2$–KCl–H_2O.

2. The system $CaCl_2$–KCl–H_2O at 35° is characterized by the retrograde solubility of potassium chloride.

CLEVELAND, OHIO RECEIVED JANUARY 2, 1946