for the system reported here. The calculation method used is similar to the one suggested by Prausnitz *et al.* (*4*).

$$\ln \gamma_1 = x_2^2 \left\{ \tau_{21} \frac{\exp(-2\alpha_{12}\tau_{21})}{[x_1 + x_2 \exp(-\alpha_{12}\tau_{21})]^2} + \tau_{12} \frac{\exp(-\alpha_{12}\tau_{12})}{[x_2 + x_1 \exp(-\alpha_{12}\tau_{12})]^2} \right\} \quad (1)$$

$$\ln \gamma_2 = x_1^2 \left\{ \tau_{12} \frac{\exp(-2\alpha_{12}\tau_{12})}{[x_2 + x_1 \exp(-\alpha_{12}\tau_{12})]^2} + \tau_{21} \frac{\exp(-\alpha_{12}\tau_{21})}{[x_1 + x_2 \exp(-\alpha_{12}\tau_{21})]^2} \right\} \quad (2)$$

where

$$\begin{aligned} \tau_{12} &= (g_{12} - g_{22})/RT \\ \tau_{21} &= (g_{21} - g_{11})/RT \\ \alpha_{12} &= 0.30 \\ g_{12} &= g_{21} \end{aligned} \quad (3)$$

Calculated values of y_1 based on τ_{12} and τ_{21} are given in Table II ($y_{1\ \mathrm{calcd}}$). The maximum percentage deviation between $y_{1\ \mathrm{exptl}}$ and $y_{1\ \mathrm{calcd}}$ = $(100\Delta y/y_{1\ \mathrm{exptl}})$ is less than 3.03%. Plots of log (γ_1/γ_2) *vs.* x_1 in accordance with the Redlich and Kister equation (*5*) showed the integrated value was 0.417 and the absolute value was 4.075. The small integrated value showed that the data were consistent.

NOMENCLATURE

g_{ij} = energies of interaction between an *i-j* pair of molecules
P° = vapor pressure, mm of Hg
x = mole fraction in liquid phase
y = mole fraction in vapor phase
α_{ij} = nonrandomness constant for binary *i -j* interactions
Δy = $(y_{1\ \mathrm{exptl}} - y_{1\ \mathrm{calcd}})$
γ = activity coefficient
π = total pressure, mm of Hg
τ_{ij} = coefficient defined in Equation 3

Subscripts

1 = carbon disulfide
2 = methanol

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Solubility Isotherm of the $FeCl_2$-$MgCl_2$-HCl-H_2O System

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The $FeCl_2$-$MgCl_2$-HCl-H_2O system at 50° C was studied at HCl concentrations of 2, 4, and 11 weight % by using a vacuum evaporation method. Experimental results were shown in a diagram by projecting the data points on the $FeCl_2$-$MgCl_2$-H_2O face, using the HCl vertex as the projection center. Within the HCl concentration ranges investigated, the solid phases existing in the system are $FeCl_2 \cdot 4H_2O$ and $MgCl_2 \cdot 6H_2O$. No double or complex salts were found.

SOLUBILITY isotherms of the $FeCl_2$-HCl-H_2O system at 40° and 60° C (*5*), the $MgCl_2$-HCl-H_2O system at 25° C (*1, 2*), and the $FeCl_2$-$MgCl_2$-H_2O system at 15° and 40° C (*3, 4*) are available in the literature. However, no data on the $FeCl_2$-$MgCl_2$-HCl-H_2O system have been reported. The present work investigated this quaternary system at 50° C.

EXPERIMENTAL

The apparatus used is shown schematically in Figure 1. An aqueous solution with the desired composition of $MgCl_2$ and HCl was saturated with $FeCl_2 \cdot 4H_2O$ at 50° ± 0.5° C. The solution was charged into flask *A* and agitated, and the pressure in the system was adjusted so that

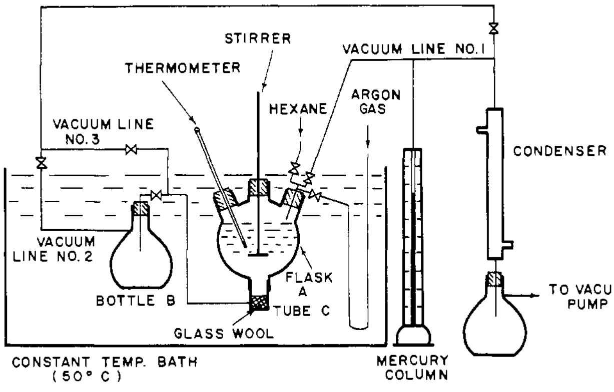

Figure 1. Schematic diagram of experimental apparatus

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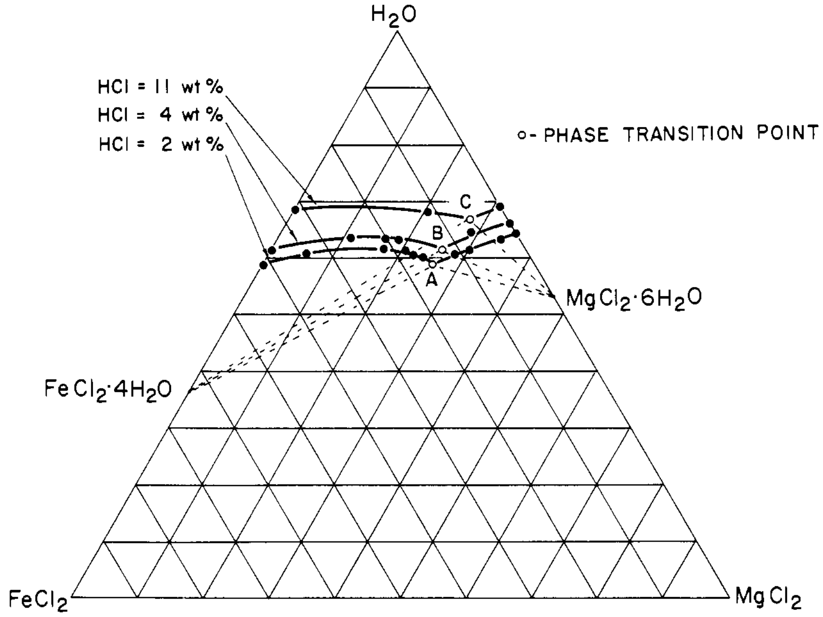

Figure 2. Projections of solubility curves on $FeCl_2$–$MgCl_2$–H_2O face

the solution boiled at 50° ± 0.1° C. At this stage, vacuum line 1 was used. When a sufficient quantity of crystals had formed, the vacuum line was switched from 1 to 2, the valve on the argon gas line was opened, and the mother liquor was sucked into bottle *B*, leaving the crystals inside tube *C*. The crystals were then washed and dried by passing hexane through tube *C* via vacuum line 3. A sample of the mother liquor was analyzed for Fe^{2+}, Mg^{2+}, and free HCl, while samples of the crystals were identified by x-ray diffraction.

The iron(II) and free HCl in the liquid samples were determined by titration with standard cerium(IV) ammonium nitrate and NaOH solution, respectively. For the determination of Mg^{2+}, the Fe^{2+} ions were first oxidized to Fe^{3+} and removed by an ion exchange column containing Dowex 1 × 8 resin,. The iron-free solution was then titrated with EDTA at a pH between 9 and 10, using Eriochrome Black T as indicator. All the end points of these titrations are sharp and the error should be less than 0.5%.

Reagent grade iron(II) chloride tetrahydrate, magnesium chloride hexahydrate, and 37.4% hydrochloric acid from the J. T. Baker Chemical Co. were used to prepare the test solutions. The iron(II) chloride tetrahydrate was purified by recrystallization before use.

RESULTS AND DISCUSSION

A four-component system is usually represented on a regular tetrahedron with the vertices corresponding to the components of the system. However, a central projection onto one of the faces of the tetrahedron may be employed. Figure 2 is a projection on the $FeCl_2$-$MgCl_2$-H_2O face, using the HCl vertex as the projection center. To represent the points of the system on Figure 2, the percentage composition was recalculated so that the sum of $FeCl_2$ + $MgCl_2$ + H_2O was taken as 100%.

As seen from Figure 2, the solubilities of $FeCl_2$ and $MgCl_2$ decrease with increasing HCl concentration. Thus, by raising the HCl concentration of a saturated solution—e.g., bubbling dry HCl gas through the solution—either $FeCl_2 \cdot 4H_2O$ or $MgCl_2 \cdot 6H_2O$ will be crystallized, depending on the crystalline region in which it is located. If the starting solution has a composition corresponding to the phase transition point, mixed crystals of $FeCl_2 \cdot 4H_2O$ and $MgCl_2 \cdot 6H_2O$ will be obtained. This means that composition corresponding to points *B* and *C* on Figure 2 may be reached by bubbling dry HCl gas through a solution with a composition corresponding to point *A*. This phenomenon was confirmed experimentally.

The solid phases found in this investigation are iron(II) chloride tetrahydrate and magnesium chloride hexahydrate only. The salts, $FeCl_2 \cdot 2H_2O$ (*5*) and $MgCl_2 \cdot HCl \cdot 7H_2O$ (*2*), and the double salt, $FeCl_2 \cdot MgCl_2 \cdot 8H_2O$ (*3*), were not detected.

Table I. Solubility in $FeCl_2$-$MgCl_2$-HCl-H_2O System at 50° C

Liquid-Phase Composition, Wt. %			
$MgCl_2$	$FeCl_2$	HCl	Solid Phase
0	40.34	2.04	$FeCl_2 \cdot 4H_2O$
5.32	33.11	2.19	$FeCl_2 \cdot 4H_2O$
16.61	21.41	2.18	$FeCl_2 \cdot 4H_2O$
19.66	18.36	2.07	$FeCl_2 \cdot 4H_2O$
21.88	17.33	2.12	$FeCl_2 \cdot 4H_2O$
23.31	15.68	1.93	$FeCl_2 \cdot 4H_2O$
25.46	14.97	1.95	$FeCl_2 \cdot 4H_2O$ + $MgCl_2 \cdot 6H_2O$
27.62	11.36	2.15	$MgCl_2 \cdot 6H_2O$
29.43	8.45	2.21	$MgCl_2 \cdot 6H_2O$
33.48	2.89	2.27	$MgCl_2 \cdot 6H_2O$
34.74	0	1.98	$MgCl_2 \cdot 6H_2O$
0	37.20	3.96	$FeCl_2 \cdot 4H_2O$
11.38	24.63	3.87	$FeCl_2 \cdot 4H_2O$
15.72	19.89	4.21	$FeCl_2 \cdot 4H_2O$
17.93	17.32	4.07	$FeCl_2 \cdot 4H_2O$
24.97	12.07	4.14	$FeCl_2 \cdot 4H_2O$ + $MgCl_2 \cdot 6H_2O$
27.35	6.12	4.19	$MgCl_2 \cdot 6H_2O$
32.30	0	4.01	$MgCl_2 \cdot 6H_2O$
0	27.70	11.00	$FeCl_2 \cdot 4H_2O$
18.31	10.40	10.86	$FeCl_2 \cdot 4H_2O$
24.60	4.75	11.24	$FeCl_2 \cdot 4H_2O$ + $MgCl_2 \cdot 6H_2O$
27.42	0 .	11.10	$MgCl_2 \cdot 6H_2O$

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