Vapor-Liquid Equilibria of the Hydrochloric Acid–Ferrous Chloride–Water System

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A simple technique for the measurement of total and partial vapor pressures of the hydrochloric acid–ferrous chloride–water system and a method to correlate vapor-liquid equilibrium data are described. The concentration ranges investigated were 2.95 to 8.18 and 0.73 to 1.28 moles per liter for HCl and $FeCl_2$, respectively. Experimental data obtained at 70° C. fit an equation relating the partial vapor pressures of the system and the mole fractions of the components. In the temperature range 50° to 90° C., the total and partial vapor pressures obey the Clausius-Clapeyron equation.

THE HCl-$FeCl_2$-H_2O system was studied because of its importance in regenerating hydrochloric acid from chloride solutions and the lack of experimental data in the literature.

APPARATUS AND PROCEDURE

The experimental apparatus was arranged as shown in Figure 1. Bottles *A*, *B*, and *C* were 500-ml. glass flasks. The mercury manometer used had a readable scale of 1 mm., and the temperature bath was kept within ±0.1° C. of the desired temperature by a dual Microtrol thermoregulator (Blue M Electric Co. Model MR-3262A-1). The argon gas was preheated in a copper coil immersed in the bath (not shown in the diagram).

The system was first allowed to come to equilibrium at the desired temperature. The air was then removed by evacuating and flushing bottles *A* and *B* with vapor several times. The total vapor pressure of the system, P_t, was measured by equalizing the pressures across the U-tube and reading this on the manometer. The partial vapor pressure of HCl, P_{HCl}, was determined by introducing argon gas to purge the vapor from *A* to *C*, where the HCl gas was absorbed and determined by titration. The partial vapor pressure of HCl was calculated as

$$P_{HCl} = NV \times 10^{-3} \times 760 \times 82.06\ T/V_t, \text{ mm. Hg}$$

where

N = normality of NaOH solution
V = volume of NaOH solution used, ml.
T = temperature, ° K.
V_t = total vapor space of bottle *A*, ml.

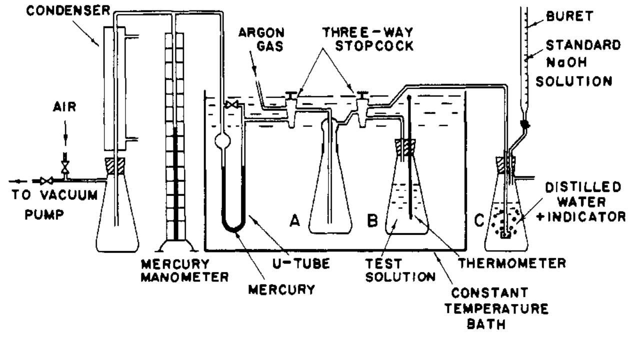

Figure 1. Schematic diagram of apparatus

The test solution was analyzed for HCl, $FeCl_2$, and $FeCl_3$ only after the experiment, since its composition can change during evacuation of the air from the system.

The free HCl was determined by titration with standard NaOH solution on a Quantitrator (Evans Electroselenium). The end point—i.e., when ferric hydroxide began to precipitate—was indicated by a sudden change in the galvanometer reading. The ferrous iron was analyzed with standard ceric ammonium nitrate using *n*-phenylanthranilic acid as an indicator, while the ferric iron was determined by first being reduced to ferrous state in a Walden silver reducer and then analyzed as above. The density of the solution was measured by a hydrometer.

Reagent-grade ferrous chloride tetrahydrate and 37.4% hydrochloric acid, both from J. T. Baker Chemical Co., and deionized water were used to prepare the test solutions, which contained a small amount of ferric iron, usually less than 1 gram per liter.

EXPERIMENTAL RESULTS

The experimental results are presented in Table I. Figures 2 and 3 show the effect of temperature on the total vapor pressure of the system and the partial vapor pressure of HCl. In these figures, the experimental data were plotted as log *P* *vs.* $1/T$ where *P* is either P_t or P_{HCl}. Both log P_t and log P_{HCl} fit well with the equation

$$\log P = A - B/T$$

where *A* and *B* are constants and a function of both the HCl and $FeCl_2$ concentrations. According to the Clausius-Clapeyron equation,

$$\log P_t = -[\Delta \bar{H}_{vap.}/2.303\ RT] + C$$

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where

$\Delta \bar{H}_{\text{vap}}$ = mean molar heat of vaporization, cal.
R = gas constant, 1.987 cal./deg.-mole
C = constant

the slope of the P_t *vs.* $1/T$ lines from Figures 2 and 3 gives $\Delta \bar{H}_{\text{vap.}}$ values of 10.57 and 10.07 kcal., respectively.

The effect of HCl concentration on P_t and P_{HCl} is shown in Figure 4. An increase in the HCl concentration increases

Table I. Experimental Data

HCl Concn., Moles/Liter	$FeCl_2$ Concn., Moles/Liter	Temp., °C.	P_t, Mm. Hg	P_{HCl}, Mm. Hg
4.52	0.73	50	61.5	0.9
		60	102.1	1.4
		60	102.1	1.3
		70	155.5	4.3
		75	193.6	5.6
		80	244.4	8.5
		90	363.8	24.5
5.43	1.50	50	51.4	8.5
		60	89.9	14.6
		70	139.0	25.9
		80	211.4	37.1
		90	353.6	79.6
2.95	0.78	70	203.7	1.0
4.36	0.78	70	189.9	4.3
5.77	0.78	70	145.6	15.3
6.40	0.78	70	140.2	32.9
7.22	0.78	70	153.7	58.8
8.18	0.78	70	191.0	92.9
5.30	1.17	70	140.2	21.2
5.30	1.28	70	135.2	21.6
5.95	1.08	70	137.7	17.2
6.06	1.09	70	150.4	24.3
6.14	1.04	70	150.4	23.5
6.44	1.06	70	150.4	26.1
2.60	0.92	70	188.5	0.5
2.60	0.92	70	188.5	0.8

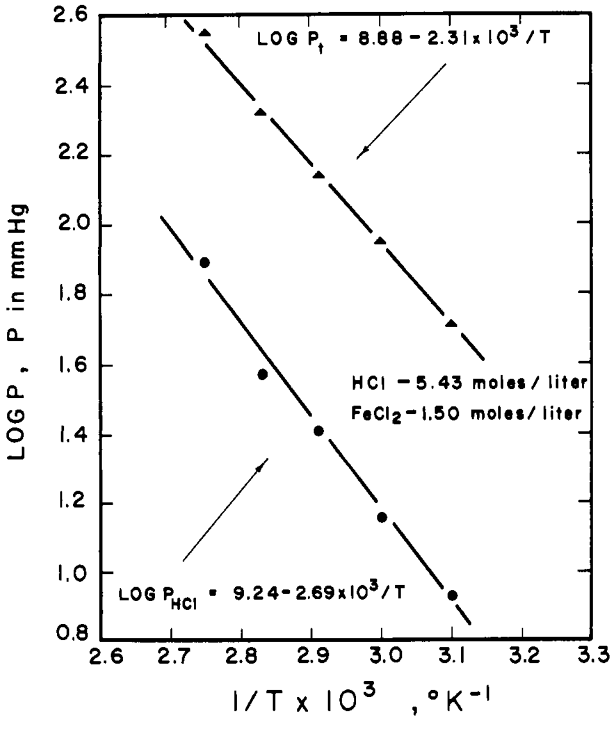

Figure 2. Diagram of log P *vs.* $1/T$

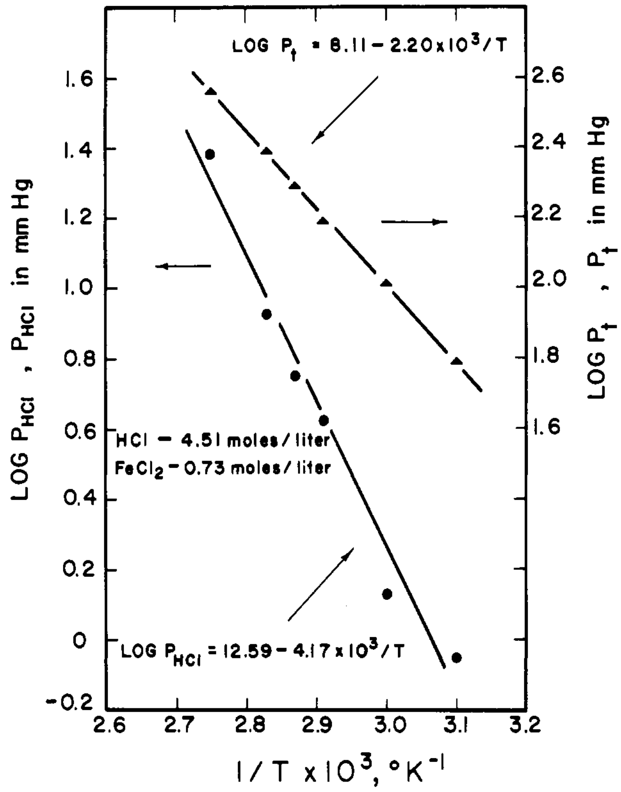

Figure 3. Diagram of log P *vs.* $1/T$

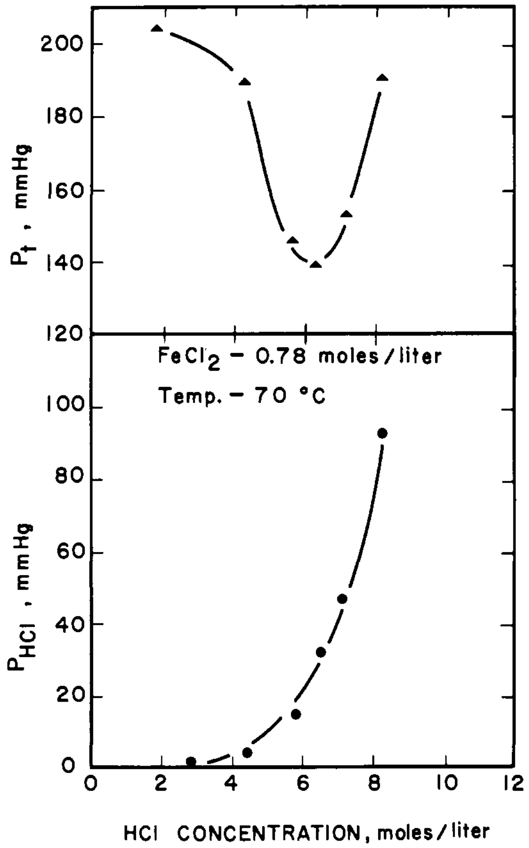

Figure 4. Effect of HCl concentration on P_t and P_{HCl}

the mean ionic activity of HCl and consequently increases P_{HCl}. On the other hand, addition of HCl to the system decreases the activity of water molecules and hence reduces the partial vapor pressure of water. The existence of a minimum point on the plot of log P_t *vs.* HCl concentration shows a negative deviation from Raoult's law.

Experimental data obtained at 70° C. are correlated by the following equation with an average absolute deviation of 12.1%. Details of the derivation are deposited with the Americal Society for Information Science.

$$\log\left[\frac{P_{\text{HCl}}}{P_t - P_{\text{HCl}}} \times \frac{x_3(2x_1 + 3x_2 + x_3)}{x_1(x_1 + 2x_2)}\right] = 21.94\,(x_1 + 3x_2)^{4/3} - 0.93$$

where x_1, x_2, and x_3 are mole fractions of HCl, $FeCl_2$, and H_2O in the solution, respectively.

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Measurement of Contact Angles Encountered during Distillation of Binary Liquids on a Copper Surface

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Contact angles are presented for the systems methanol-water, *n*-heptane–methylcyclohexane, acetone-water, *n*-heptane–toluene, benzene-cyclohexane, ethanol-water, 1-propanol–water, and benzene–*n*-heptane in contact with a copper surface, measured under conditions of distillation both at total reflux and at equilibrium.

A CONSIDERABLE amount of published data exists listing angles of liquids in contact with a variety of solid surfaces measured over a range of temperatures in the presence of air or saturated vapor-air mixtures. However, only scant information is available in the literature (*2*, *3*, *4*) where contact angles have been measured under conditions which are most frequently encountered in chemical engineering operations—namely, distillation, absorption, or heat transfer. The systems examined in this investigation are of commercial importance, and the difficulty of separation by distillation has been attributed generally to the reduction of surface area produced by the changes in surface properties (*5*). When a liquid mixture is distilled, the liquid and vapor exchange may cause an increase or decrease in the surface tension. For some systems these changes can be significant, and the performance of a packed distillation column is influenced considerably by these changes. A system is declared to be positive if its surface tension value increases down the column and negative if the value decreases. A decrease in surface tension will enhance the wetting of a packing, while an increase in surface tension results in a reduction of the effective wetted area.

The determination of the contact angles now presented is of prime importance in understanding the role of surface properties on transport in packed columns.

EXPERIMENTAL

The designs of apparatus employed for determining the contact angles are shown in Figures 1 and 2, and are developments of designs described previously by Ponter *et al.* (*2*).

Contact Angle for Liquids in Equilibrium with Their Surrounding Vapor. The apparatus shown in Figure 1 consisted essentially of a 1-liter flask, an observation cell, and a cold finger condenser. The flask was fitted with a thermometer pocket and a condensate return line, and was heated with a 300-watt Isomantle. The observation cell (15 cm. × 10 cm. o.d.) comprised two sections, the lower section being fitted with two optical flats situated on opposite sides of the cell. The copper plate was supported by the glass structure above the central vapor line from the flask. The upper section was fitted with a thermometer pocket, a vapor exit line to the condenser, and a hollow rubber plug to allow the introduction of a sessile drop via a hypodermic needle. The cell sections were fitted with electrical heaters and lagged with asbestos to minimize heat losses.

The copper surface was carefully prepared by polishing to a surface roughness of 6 microns, degreasing, and finally washing in the fluid under test, before being introduced to the cell. Care was taken to ensure that the plate was horizontal. To achieve this, the vertical cross wire in the travelling microscope was aligned against a thin plumb line. The goniometer eyepiece was then rotated through 90° and the specimen plate adjusted until its surface lay parallel to the new position of the cross wire. Variations of plate inclination of up to ½ degree to the horizontal did not affect the value of contact angle obtained. A period of 3 hours was then allowed for the system to come to