mixtures investigated, whereas $k_1$ takes different values depending upon the system under discussion. These results clearly indicate the presence of a correlation between $\Delta V$ and $\Delta n$. This is not unexpected because $\Delta V$, which is the deviation from volume additivity, i.e., ideality, can be considered as a measure of interaction between the components and $\Delta n$, which is closely related to the change in molecular polarizabilities on mixing of the components,[4] is also a barometer of interaction between the components.

The following general tendencies concerning $\Delta V$ and $k_1$ are recognized from those tables: (1) The values of $k_1$ are small in EtOEtOH-$H_2O$ and *i*-BuOEtOH-$H_2O$ systems but large in PrOEtOH-$H_2O$ and EtOPrOH-$H_2O$ systems. (2) The values of $\Delta V$ are small in BuOEtOH-$H_2O$ and *i*-BuOEtOH-$H_2O$ systems but large in EtOEtOH-$H_2O$ and *i*-PrOEtOH-$H_2O$ systems. (3) The methoxy group induces larger changes in $\Delta V$ than the ethoxy group. (4) Isoalkoxyethanol-water systems have larger values of $\Delta V$ than *n*-alkoxyethanol-water systems. On the contrary, the former systems have smaller values of $k_1$ than the latter systems. (5) It is reported that the ability of forming an intramolecular hydrogen bond is larger in MeOPrOH than in MeOEtOH and in EtOPrOH than in EtOEtOH.[11] The values of $\Delta V$ are smaller in the MeOPrOH-$H_2O$ system than in the MeOEtOH-$H_2O$ system and smaller in the EtOPrOH-$H_2O$ system than in the EtOEtOH-$H_2O$ system. On the other hand, the value of $k_1$ is larger in the MeOPrOH-$H_2O$ system than in the MeOEtOH-$H_2O$ system and larger in the EtOPrOH-$H_2O$ system than in the EtOEtOH-$H_2O$ system. The intramolecular hydrogen bonding ability of molecules seems to have great influence on not only $\Delta V$ but also $\Delta n$.

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# Solubility of Cuprous Chloride in Aqueous Hydrochloric Acid Solutions†

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**The solubilities of cuprous chloride in water and hydrochloric acid solutions were determined at different temperatures. Effects of temperature and hydrochloric acid concentration on the solubility were correlated by the equation $\ln S = a + b/T + c \ln (1 + dX)$ where $S$, $X$, and $T$ are respectively solubility, concentration of hydrochloric acid, and temperature in K, and $a$, $b$, $c$, and $d$ are constants.**

## Introduction

Solubilities of sparingly soluble solids in liquids are often required in studies on mass transfer in solid-liquid systems. Such data are also important in systems where gas absorption in slurries is followed by its reaction with a simultaneously dissolving solid. The present studies on the solubility of CuCl in aqueous HCl solutions were undertaken in view of their importance in a number of reactions, such as in the reactions of acetylene (*1*) and of oxygen (*3*) with cuprous chloride.

The solubility of CuCl in water was studied in the temperature range 20-50 °C. The effect of HCl concentration at various temperatures was also investigated.

## Experimental Section

The solubility experiments were carried out in a magnetically stirred vessel provided with a jacket for circulating water at constant temperature. A constant temperature (±0.1 °C) was maintained using a thermostatic bath.

Table I. Solubility Data for the CuCl-HCl-$H_2O$ System

| concn of HCl, g-mol/L | solubility of CuCl, $S \times 10^2$, g-mol/L | | | |
|---|---|---|---|---|
| | 20 °C | 29 °C | 40 °C | 50 °C |
| 0.0 | 0.295 | 0.380 | 0.519 | 0.668 |
| 0.129 | 0.944 | 1.175 | 1.603 | 1.927 |
| 0.158 | 1.122 | 1.380 | 1.884 | 2.238 |
| 0.266 | 1.698 | 2.113 | 2.985 | 3.467 |
| 0.398 | 2.398 | 2.985 | 4.121 | 4.897 |
| 0.603 | 3.388 | 4.168 | 5.888 | 6.839 |

Freshly prepared cuprous chloride stored in a vacuum desiccator was used throughout the work. High-purity nitrogen gas, passed through a pyrogallol solution, was used for flushing purposes. Reagents used for analysis were of AR grade.

In a typical run, the jacketed vessel was thoroughly flushed with nitrogen, and 100 mL of degassed, distilled water was charged with an excess of cuprous chloride. Nitrogen gas was constantly kept bubbling through the slurry, which was magnetically stirred using a Teflon-coated needle. A constant temperature was maintained in the vessel by circulating water through the outer jacket, from a thermostat set at the required temperature.

Samples were withdrawn at intervals of 5-10 min for analysis, and this was continued until saturation was indicated by constancy of two to three consecutive readings. Dissolved cuprous chloride in the samples was analyzed by a method described by Vogel (*2*).

In all the experiments, precautions were taken to maintain an oxygen-free atmosphere throughout, since cuprous chloride

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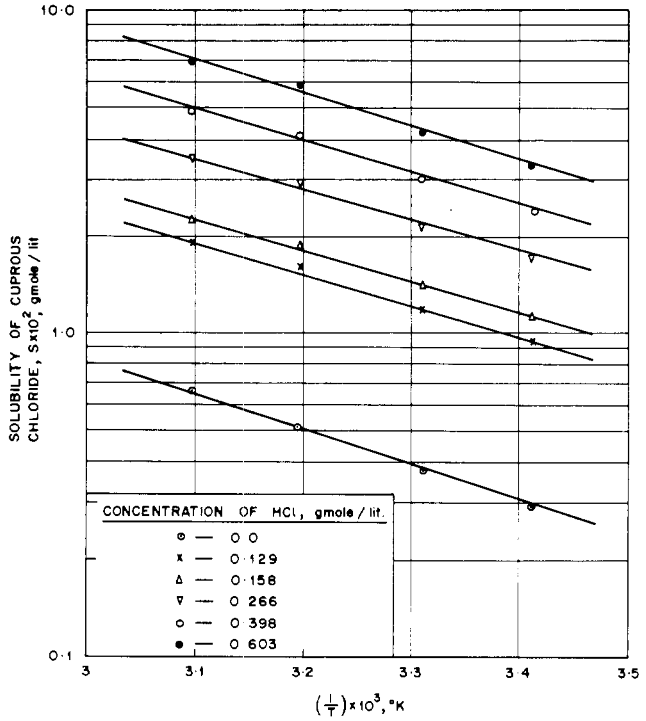

Figure 1. Temperature dependence of solubility of cuprous chloride.

is highly reactive in the presence of oxygen to form soluble cupric salts.

## Results and Discussion

Solubilities of cuprous chloride in water and HCl solutions were determined at 20, 29, 40, and 50 °C. The concentration of HCl was varied from 0.129 to 0.603 g-mol/L. The data are presented in Table I. An experimental error in the solubility values estimated by repeating a single experiment three to four times was found to be less than 5%.

Various empirical equations were used to correlate the data and to obtain a relationship between solubility, temperature, and concentration of HCl. The following equation was found to represent the data most satisfactorily:

Table II. Results of Regression Analysis

| parameter | value |
|---|---|
| $a$ | 2.2265 |
| $b$ | $-2.3480 \times 10^3$ |
| $c$ | 1.0486 |
| $d$ | 15.0 |
| $\Delta H$ | 4.696 kcal/g-mol |
| stand dev, $\sigma$ | $1.1513 \times 10^{-3}$ |

$$\ln S = a + b/T + c \ln (1 + dX) \qquad (1)$$

where $S$ and $X$ are respectively solubility of cuprous chloride and concentration of HCl in g-mol/L, $T$ is temperature in K, and $a$, $b$, $c$, and $d$ are constants.

In order to obtain the best fit, regression analysis was carried out. The values of the constants $a$, $b$, $c$, and $d$ and the temperature-dependent heat of solution, $\Delta H$, are given in Table II. The solubility values estimated from eq 1, using the constants in Table II, and the experimental data agree within 2–5%. The Arrhenius type of temperature dependence of solubility is also evident from Figure 1, which is a plot of ln $S$ vs. $1/T$.

## Glossary

| | |
|---|---|
| $a$, $b$, $c$, $d$ | constants in eq 1 |
| $\Delta H$ | temperature-dependent heat of solution, kcal/g-mol |
| $S$ | solubility of cuprous chloride, g-mol/L |
| $T$ | temperature, K |
| $X$ | concentration of hydrochloric acid, g-mol/L |
| $\sigma$ | standard deviation |

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# Surface and Interfacial Tensions of Conjugate Solutions in Ternary Systems

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**A high-precision apparatus was constructed to measure surface and interfacial tensions of liquids by the pendent-drop technique. The method as used in this work requires control of temperature, photographic recording of the drop, precise measurement of dimensions, and the use of a computer to determine the surface tensions from the data input. The surface and interfacial tensions of conjugate solutions of compositions located in the isothermal miscibility gap of two ternary systems were measured. The systems investigated were benzene–water–ethanol and *n*-hexane–water–ethanol at 20.0 °C.**

Knowledge of wetting and spreading is important to engineers in the design of liquid–liquid contact operations wherever matter passes across an interface. For this purpose not merely the interfacial tension but also the surface tensions of the two fluids are required. Such information is recorded for few ternary systems (*1–4*). Brun (*1–3*) measured the surface and interfacial tensions of conjugate phases in the water–3-methyl-1-butanol–ethanol system by the method of rising drops; he found that the surface tensions of the conjugate phases approach each other and become equal at the plait point and that the interfacial tension falls to zero at the same point (as would be expected). Murphy, Lastovica, and Fallis (*4*) report surface and interfacial tensions determined by the ring method for several ternary

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