Solubility of Chloramine in Organic Liquids

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The solubility of chloramine in *n*-heptane, cyclohexane, carbon tetrachloride, benzene, and chloroform is determined experimentally at 25°C. The data are used to predict the solubility of chloramine in methyl ethyl ketone. The method is applied to calculate the solubility of ammonia in methyl ethyl ketone, and the predicted value is compared with the experimental data.

The solubility of gases in different solvents is an important piece of information needed in testing the applicability of various gas-liquid mass-transfer models, both for reacting and nonreacting systems and in the design of mass-transfer equipment. Chloramine is an important intermediate in the synthesis of diazacyclopropane from ammonia, chlorine, and a carbonyl compound (aldehyde or ketone) (*7*).

In studies on gas-liquid reactions leading to the formation of 3-methyl-3-ethyl diazacyclopropane reported elsewhere (*4*), it was necessary to know the solubility of chloramine in methyl ethyl ketone. Attempts to experimentally determine the solubility of chloramine in methyl ethyl ketone were not successful because of its unstable nature and high reactivity (*5–7*). The generalized correlations available in the literature (*8, 10*) for the estimation of the solubilities of gases in liquids are applicable to nonreacting and single solute–solvent systems. Chloramine generated in the present work was always accompanied by excess ammonia and nitrogen; further, chloramine reacts with ketones especially in the presence of ammonia. Therefore, an indirect method used to determine the solubility of chloramine in methyl ethyl ketone is presented in this paper.

Basis of method. The solubility of a given gas in terms of mole fraction of the solute bears a semilogarithmic relation with the square of the solubility parameter of the solvent (*3*). Therefore, the results of the experiments conducted to determine the solubility of chloramine in a few organic solvents were used to calculate the solubility of chloramine in methyl ethyl ketone by using the solubility parameter of methyl ethyl ketone.

Experimental

Materials. Analytical reagent-grade solvents *n*-heptane, benzene, carbon tetrachloride, cyclohexane, and chloroform were used for experimentation.

Chloramine, being unstable, was not readily available. It was generated in an apparatus similar to that described by Sisler et al. (*9*) by reacting chlorine (diluted with nitrogen) and ammonia. The gases were dried by suitable means before they entered the apparatus. Based on the preliminary experiments, the following conditions for experimentation were fixed.

Temperature of chloramine generator	110°C
Flow rate of chlorine	0.1133 mol/hr
Flow rate of ammonia	1.8128 mol/hr
Flow rate of nitrogen	0.5080 mol/hr

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Under the conditions specified, the chloramine yield (based on chlorine) was 72.7%. This results in a partial pressure of 0.0342 atm (with respect to chloramine) in the stream of gases leaving the chloramine generator and subsequently entering the solubility cell.

Apparatus. The solubility studies were conducted in an apparatus shown in Figure 1. Its essential features are measuring devices for the three gases, chloramine generator, and solubility cell. Capillary flow meters previously calibrated were used to measure the flow rates of the gases. The chloramine generator used in the present work is essentially similar in design to that described by Sisler et al. (*9*).

The solubility cell was made of a glass tube 4.5 cm i.d. and 20 cm long, provided with a jacket to circulate a fluid to maintain isothermal conditions; a stirrer to keep the contents of the vessel well mixed; a provision to collect the samples with a hypodermic syringe; and provisions for introduction and removal of gases and liquid. The temperature was controlled within ±0.1°C. The stirrer was designed in accordance with the specifications of Cooper et al. (*1*) to provide good mixing and connected to a motor through a liquid seal containing glycerine. The gases (chloramine, ammonia, and nitrogen) entered the cell very near the bottom of the cell through a 6-mm glass tube. The exit gases passed through the absorption unit before being vented to atmosphere.

Analysis of chloramine. Chloramine was analyzed by the iodometric method (*2*). The equation representing the reaction is

$$NH_2Cl + 2H^+ + 2I^- \rightarrow NH_4^+ + I_2 + Cl^- \qquad (1)$$

The iodine thus generated is titrated with standard sodium thiosulfate solution with starch as the indicator. Chloramine present in the solution was estimated from the amount of iodine liberated.

Procedure. A measured amount of the solvent was taken in the solubility cell maintained at 25° ± 0.1°C. The flow rates of chlorine, ammonia, and nitrogen were adjusted to the desired values. Chloramine formed in the chloramine reactor along with unreacted ammonia, and

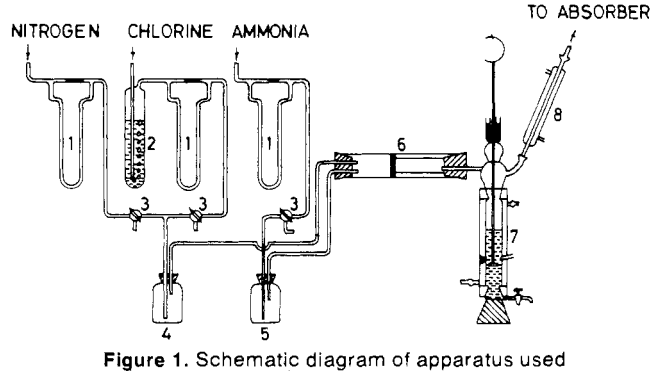

Figure 1. Schematic diagram of apparatus used

1. Capillary flow meter
2. Sulfuric acid bubbler
3. Three-way stopcock
4. Mixing bottle for chlorine and nitrogen
5. Trap in ammonia line
6. Chloramine generator
7. Solubility cell
8. Condenser

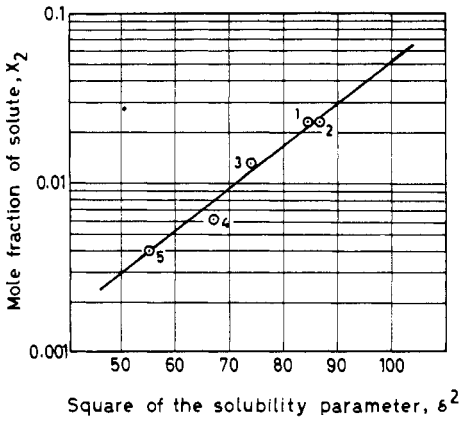

Figure 2. Solubility of chloramine in different solvents as function of solubility parameter

1. Benzene
2. Chloroform
3. Carbon tetrachloride
4. Cyclohexane
5. Heptane

Table I. Solubility of Chloramine in Various Solvents at 25°C

Solvent	Solubility parameter (cal/cc)$^{1/2}$	Mole fraction of solute Exptl	Calcd	% Dev[a]
Chloroforrn	9.3	0.0229	0.0241	−5.2
Carbon tetrachloride	8.6	0.0131	0.0118	9.9
Benzene	9.2	0.0224	0.0217	3.1
Cyclohexane	8.2	0.0060	0.0080	33.3
n-Heptane	7.4	0.0040	0.0040	0.0
			Average	10.3

[a] % Deviation = $\frac{\text{Exptl value} - \text{calcd value}}{\text{Exptl value}} \times 100.$

nitrogen was passed into the solvent, keeping the solvent well stirred. Samples were collected at different time intervals, and chloramine was analyzed in the manner described above. The experiment was conducted until the concentration of chloramine in three or more consecutive samples was the same.

Results and Discussion

The solubility data obtained at 25°C in different solvents are given as a plot of the square of the solubility parameter of the solvent vs. logarithm of the mole fraction of the solute in Figure 2. The data shown in Table I fitted the relation

$$\log x_2 = 0.0247\,\delta_T^2 - 3.7537 \qquad (2)$$

with an average absolute deviation of 10.3%. With the solubility parameter of methyl ethyl ketone at 25°C in Equation 2, x_2 was 0.0226. This is equivalent to 2.547×10^{-4} g mol/cc of the solvent. The solubilities at different temperatures were calculated by first calculating the solubility parameter at different temperatures and by using Equation 2.

Henry's law constants at different temperatures for chloramine in methyl ethyl ketone obtained by using the relation

$$P_c = C_c{}^* H_c \qquad (3)$$

followed the equation

$$\log H_c = -\frac{698.7}{T} + 4.4938 \qquad (4)$$

with a maximum deviation of 4.2% and an average absolute deviation of 2.4%.

To ensure that this method gives reliable results, the solubility of ammonia in different solvents was obtained, and a figure similar to Figure 2 was made. With this plot the solubility of ammonia in methyl ethyl ketone was 0.103 against an experimental value of 0.098. This showed that it is possible to predict the solubility of a gas, particularly when it reacts with the solvent by this method. The solubility of chloramine in methyl ethyl ketone thus obtained was used to predict reaction rates (*4*), and the predicted values agreed well with the experimental values. This shows that an indirect method such as the one used here to find the solubility could be used with advantage in the case of systems where the solute and the solvent undergo chemical reaction.

Nomenclature

$C_c{}^*$ = equilibrium concentration of chloramine, g mol/cc
H_c = Henry's law constant (atm) (cc)/g mol
P_c = partial pressure of chloramine, atm
T = temperature, K
x_2 = mole fraction of the solute
δ_T = solubility parameter of the solvent at temperature T (cal/cc)$^{1/2}$

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