

contributions from solute translational entropies in both phases cancel. The values obtained from the present work are close to those derived from the data of the other workers in those cases where comparisons are possible (ethylbenzene and *n*-hexylbenzene).

Abraham (23) recently investigated data for the hydration process in several homologous series, including *n*-alkylbenzenes. He documented the existence of linear relations between the standard molar free energies, enthalpies, and entropies of hydration and the number of carbon atoms, and concluded that methylene increments for the free energies and enthalpies vary among series. Figures 2 and 3 show that our free energy and enthalpy values for the series ethylbenzene through *n*-hexylbenzene combined with literature values (21) for toluene display these linear relations within experimental error. The points for benzene, however, lie off the lines as might be expected from an end effect in the series. From regression of the data for toluene through *n*-hexylbenzene against chain length *N* we obtained the intercepts *a* and methylene increments (slopes) *b* listed in Table V. The table also lists methylene increments obtained by Abraham (23) using other data. Our value for the methylene increment of the free energy of hydration in *n*-alkylbenzenes (0.75 kJ mol^{-1}) is 23% higher than that obtained by Abraham, but is close to the value (0.74 kJ mol^{-1}) which he calculated for the methylene increment in lower members of the *n*-alkane series (ethane through *n*-octane). Our values for the methylene increments of enthalpy and entropy also agree within experimental uncertainty with those given by Abraham for both *n*-alkylbenzenes (Table V) and alkanes. Thus Abraham's conclusion that methylene increments differ from one homologous series to another may be premature, since the values of these increments are sensitive to the accuracy of the solubility data.

Registry No. Ethylbenzene, 100-41-4; *n*-propylbenzene, 103-65-1; *n*-butylbenzene, 104-51-8; *n*-pentylbenzene, 538-68-1; *n*-hexylbenzene, 1077-16-3.

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Henry Constant of Molecular Chlorine in Aqueous Solution

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The gas-liquid phase equilibrium for molecular chlorine absorbing into aqueous solution was measured directly under conditions ($\text{pH} \approx 1$) such that only minimal corrections were necessary to adjust for chlorine hydrolysis. The Henry constant for Cl_2 at 20°C and zero ionic strength was observed to be $13.57 \text{ atm}\cdot\text{L}\cdot\text{mol}^{-1}$. The Henry constant was approximately twice as great at 30°C as at 10°C , corresponding to an enthalpy of dissolution of $26.7 \text{ kJ}\cdot\text{mol}^{-1}$. The Henry constant increased with increasing NaCl concentration, in a manner consistent with the salting-out effect. However, increasing the concentration of HCl in solution caused the opposite effect: the chlorine solubility increased, resulting in a decrease of the Henry constant for Cl_2 .

Introduction

Accurate data on the air-water phase equilibrium of molecular chlorine has important applications in water treatment in the design of chlorine supply systems (1) and of chlorine dioxide

generators (2, 3). In supplying chlorine for water treatment, molecular chlorine often is used in gaseous form and must be transferred from the gas phase into aqueous solution. Accurate knowledge of the equilibrium concentration of molecular chlorine at the air-water interface is essential to calculate the mass-transfer driving force.

It is important to distinguish between molecular chlorine solubility (i.e., the inverse of the Henry constant for Cl_2 , in appropriate units) and total chlorine solubility. Dissolved molecular chlorine in aqueous solution rapidly undergoes hydrolysis to form hypochlorous acid, thus increasing the solubility to values exceeding that of molecular chlorine. Previous researchers (4, 5) have estimated the Henry constant of Cl_2 by correcting total chlorine solubility data (the sum of molecular chlorine, hypochlorous acid, and hypochlorite ion) to adjust for the effect of chlorine hydrolysis. In order to determine the Henry constant for chlorine from such data, the chlorine hydrolysis equilibrium constant, the final solution pH, and the final chloride ion concentration must be known accurately. However, compilations of chlorine solubility given in widely used handbooks (1, 6) lack some of the information on conditions (pH, chloride concentration) needed to infer values of the Henry constant for molecular chlorine. In this study, the liquid-phase molecular chlorine concentration was determined directly, obviating the

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need to compensate for chlorine hydrolysis in interpreting the results.

The equilibrium liquid-phase chlorine concentration can be related to the gas-phase chlorine composition by Henry's law

$$p_A = HA^* \quad (1)$$

where p_A = partial pressure of chlorine in the gas phase (atm), H = Henry constant [$\text{atm}\cdot\text{L}\cdot\text{mol}^{-1}$], and A^* = equilibrium concentration of molecular chlorine in the liquid phase [$\text{mol}\cdot\text{L}^{-1}$]. Henry's law generally is a valid approximation for nondissociating solutes in dilute solution (solute mole fraction in the liquid phase less than 0.01), when the partial pressure is far removed from its critical pressure, e.g., less than 10 atm (7). These conditions are applicable to chlorine in aqueous solution at ambient pressure.

The Henry constant is an increasing function of temperature, or conversely, the solubility of a gas decreases with increasing temperature. This temperature dependence is given by (8)

$$d(\ln H)/d(1/T) = -\Delta H^\circ/R \quad (2)$$

where ΔH° is the enthalpy of dissolution ($\text{J}\cdot\text{mol}^{-1}$), i.e., for the process $\text{Cl}_2(\text{aq}, 1 \text{ M}) \rightarrow \text{Cl}_2(\text{g}, 1 \text{ atm})$; R is the universal gas constant ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), and T is the absolute temperature (K).

The Henry constant is also a function of the absorbing solution composition. In solutions of electrolytes the Henry constant can be estimated as a function of ionic strength I by the method of van Krevelen and Hofstijzer (9)

$$\log(H/H_0) = hI \quad (3)$$

where H_0 is the value of H at zero ionic strength and h is an empirical constant, referred to as the salting-out parameter.

The salting-out parameter, h , is the arithmetic sum of empirical parameters, h_+ , h_- , and h_g , which are specific for the cations, anions, and dissolved gas, respectively. It is assumed that the change in h with temperature is confined to h_g (8). In solutions of mixed electrolytes, log additivity of the individual salting-out effects can be used (10)

$$\log(H/H_0) = h_1I_1 + h_2I_2 + \dots \quad (4)$$

Experimental Conditions

Chlorine solubility experiments were performed at 10, 20, and 30 °C over a range of liquid-phase ionic strengths in order to determine the equilibrium liquid-phase chlorine gas concentration. Chlorine solubility was determined by measurement of the total chlorine concentration of an absorbing fluid of known ionic strength. The gas phase in contact with the absorbing fluid was pure chlorine gas. All experiments were performed at atmospheric pressure.

The chlorine solubility experiments were performed using a water-jacketed gas saturator bottle equipped with a septum-covered sample port near the bottom of the bottle. The gas saturator bottle was filled with 250 mL of the test solution (approximately 15 cm in depth), allowed to equilibrate to the experimental temperature, and a chlorine gas flow of 25 standard $\text{L}\cdot\text{min}^{-1}$ was allowed to pass through the solution. A preliminary experiment showed that the concentration of chlorine in the test solution was at equilibrium with the gas phase after 5 min of gas flow. In subsequent experiments, samples were taken approximately 10 min after the initiation of gas flow. Samples of the liquid in the gas saturator bottle were taken through the septum-covered sample port in the bottle. The chlorine gas was turned off momentarily and the fluid was allowed to quiesce before sampling. Samples were taken in triplicate with a gas-tight syringe (Hamilton Model 1000) and analyzed by amperometric titration for chlorine using a procedure described elsewhere (11). The coefficients of variation for the triplicate sets generally were on the order of 1%.

Table I. Solubility^a of Chlorine in Aqueous Hydrochloric Acid

temp, °C	ionic strength, ^b M			
	0.096	0.480	0.960	1.920
10	0.1104	0.1139	0.1170	0.1290
20	0.0747	0.0762	0.0792	0.0859
30	0.0531	0.0538	0.0560	0.0609

^aChlorine, M, at 101 kPa pressure of pure chlorine gas. ^bIonic strength due to hydrochloric acid only.

Table II. Solubility^a of Chlorine in Aqueous Sodium Chloride

temp, °C	ionic strength, ^b M					
	0.0	0.1	0.4	0.9	1.9	4.96
10	0.1104	0.1077	0.1025	0.0934	0.0778	0.0439
20	0.0747	0.0736	0.0688	0.0640	0.0534	0.0307
30	0.0531	0.0515	0.0489	0.0447	0.0379	0.0222

^aChlorine, M, at 101 kPa (1 atm) pressure of pure chlorine gas. ^bIonic strength due to sodium chloride only; all solutions also contain 0.096 M HCl.

Table III. Henry Constants for Chlorine as a Function of Ionic Strength Due to Hydrochloric Acid

temp, °C	H_0 , ^a atm·mol ⁻¹ ·L	$h(\text{HCl})$, L·mol ⁻¹	r^2
10	9.17	-0.0369	0.99
20	13.57	-0.0340	0.99
30	19.16	-0.0338	0.98

^a H_0 = Henry constant for chlorine at zero ionic strength.

In one set of solubility experiments, the ionic strength of the absorbing solution was varied by adjusting the hydrochloric acid concentration from 0.096 to 1.920 M. In a second set of solubility experiments, the hydrochloric acid concentration was maintained at a constant 0.096 M concentration ($\text{pH} \approx 1$) and the ionic strength was varied by adjusting the sodium chloride concentration from 0.0 to 4.96 M.

In both sets of solubility experiments, the hydrochloric acid served to suppress the chlorine hydrolysis reaction. Small corrections for hydrolysis were made for the lowest ionic strength solutions using the chlorine hydrolysis equilibrium values of Connick and Chia (12). The magnitude of this correction amounted to less than 3% of the total chlorine concentration in the most extreme case.

Results

The observed values of chlorine solubility in hydrochloric acid solution are shown in Table I. The results of chlorine solubility in the hydrochloric acid-sodium chloride solutions are shown in Table II.

Effect of Temperature. The zero ionic strength Henry constants for chlorine were determined at 10, 20, and 30 °C from regression analysis of the data presented in Table I. Regressions of $\log(H)$ on ionic strength, with hydrochloric acid only, yielded the regression parameters shown in Table III, where H_0 is the antilog of the regression equation intercept; $h(\text{HCl})$, the salting-out parameter for hydrochloric acid, is the slope of the regression line, and r^2 is the coefficient of determination.

The results from this study are compared with the results of Whitney and Vivian (4) in Table IV. Whitney and Vivian (4) determined the total solubility of chlorine in unbuffered distilled water. The chlorine solubility values of Whitney and Vivian (4), shown in Table IV, have been corrected for chlorine hydrolysis by using the equilibrium values of Connick and Chia (12) to yield the chlorine Henry constants at zero ionic strength, H_0 . To illustrate the effect of chlorine hydrolysis on the total solubility of chlorine, for the data of Whitney and Vivian (4) at 20 °C, 28% of the total chlorine present in solution was in the hy-

Table IV. Effect of Temperature on the Henry Constant for Chlorine

temp, °C	Henry const, atm·L·mol ⁻¹	
	present study ^a	Whitney and Vivian (4)
10	9.2	8.9
15	11.2	10.9
20	13.6	13.2
25	16.1	16.2
30	19.2	

^a Values calculated from regression of $\ln(H)$ vs. $(1/T)$.

dolyzed form as hypochlorous acid. Results from the present study required corrections of less than 3% to the total chlorine solubility to determine the concentration of dissolved chlorine gas. Therefore, inaccuracies in the chlorine hydrolysis equilibrium constant as reported by Connick and Chia (12) would influence the Henry constants calculated from the data of Whitney and Vivian (4) to a much greater extent than the values determined in this study. Connick and Chia (12) estimated the error in their equilibrium constants to be on the order of 1%. Whitney and Vivian (4) estimated the error in their total chlorine solubility measurements to be on the order of 2%. The agreement between the results of Whitney and Vivian (4) and those of the present study is quite good, considering the magnitude of correction required to the data of Whitney and Vivian to determine the molecular chlorine gas solubility.

When the results from the present study are used, the enthalpy of dissolution, ΔH° , of chlorine gas as calculated from the derivative of $\ln(H_0)$ with respect to $1/T$ is 26.7 kJ·mol⁻¹. This agrees closely with the value reported by Brian et al. (13), 26.4 kJ·mol⁻¹, which they calculated from the data of Whitney and Vivian (4) and Jakowkin (14).

Effect of Ionic Strength. The effect of ionic strength on the Henry constant for chlorine was investigated in two different electrolyte systems. The results from experiments in which the solution ionic strength was due entirely to added hydrochloric acid have been discussed above and are shown in Table III.

The second electrolyte system consisted of solutions of 0.096 M hydrochloric acid, to which were added increasing concentrations of sodium chloride. The log additivity of individual salting-out effects in mixed electrolyte systems has been reviewed by Schumpe et al. (10), who reported that this semi-empirical law is valid for a wide variety of electrolytes, including sodium chloride and hydrochloric acid. In this electrolyte system, the effect of increasing ionic strength due to sodium chloride can be determined while suppressing the chlorine hydrolysis reaction with the added hydrochloric acid. Since the background hydrochloric acid ionic strength was the same for all solutions in this experiment, the slope of the regression equation of $\log(H)$ vs. ionic strength is simply the salting-out parameter for the chlorine gas-sodium chloride system. The intercept of this regression is the chlorine Henry constant for 0.096 M hydrochloric acid.

The results of regressions of $\log(H)$ vs. ionic strength due to sodium chloride are shown in Table V, where $h(\text{NaCl})$ is the salting-out parameter for sodium chloride, H_0 is the zero-ionic-strength Henry constant for chlorine gas, and $h(\text{Cl}_2)$ is the empirical salting-out parameter for chlorine gas calculated from h by using the values of -0.0183 and 0.3416 for $h_+(\text{Na}^+)$ and $h_-(\text{Cl}^-)$, respectively, as given by Onda et al. (15).

The positive sign of $h(\text{NaCl})$ is consistent with the familiar "salting out" effect, according to which the aqueous solubility of a nondissociating solute decreases with increasing ionic strength. On the other hand, the negative sign of $h(\text{HCl})$ indicates increasing chlorine solubility with increasing concentration of HCl. This seemingly anomalous effect of HCl is consistent with the unusual properties of HCl and other halogen acids in aqueous solution (16)—namely, the extraordinarily high value of the hydration parameter (8.0 for HCl) and the strong increase

Table V. Henry Constant for Chlorine as a Function of Ionic Strength Due to Sodium Chloride

temp, °C	H_0^a atm·mol ⁻¹ ·L	$h(\text{NaCl})$, L·mol ⁻¹	$h(\text{Cl}_2)$, L·mol ⁻¹	r^2
10	9.17	0.0805	-0.243	0.99
20	13.57	0.0777	-0.246	0.99
30	19.16	0.0755	-0.248	0.99

^a H_0 = Henry constant for chlorine at zero ionic strength.

of the activity coefficient γ_{HCl} with increasing concentration, as well as the solvent characteristics common to strong acids such as HCl and H₂SO₄.

Summary and Conclusions

The vapor-liquid equilibrium of molecular chlorine was studied under conditions relevant to water treatment. The experiments were conducted under conditions such that only minimal corrections were required to compensate for chlorine hydrolysis; hence the determinations in this work are believed to be inherently more accurate than previously reported data.

The Henry constant for molecular chlorine at 20 °C and zero ionic strength was found to be 13.57 atm·L·mol⁻¹. The dependence on temperature was in accordance with a van't Hoff relation, with the enthalpy of dissolution equal to 26.7 kJ·mol⁻¹. Increasing the ionic strength with sodium chloride depressed the chlorine solubility. The solubility at 1 M NaCl was approximately 20% less than at infinite dilution.

Glossary

A^*	liquid-phase concentration of molecular chlorine in equilibrium with the gas phase
H	Henry constant, atm·mol ⁻¹ ·L
H_0	Henry constant at zero ionic strength, atm·mol ⁻¹ ·L
ΔH°	enthalpy change of dissolution, kJ·mol ⁻¹
h	salting-out parameter, L·mol ⁻¹
I	ionic strength, mol·L ⁻¹
p_A	partial pressure of chlorine in the gas phase, atm
R	universal gas constant = 8.314 J·K ⁻¹ ·mol ⁻¹
T	temperature, °C or K

Registry No. HCl, 7647-01-0; NaCl, 7647-14-5; Cl₂, 7782-50-5.

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