(5) Abrams, D. S.; Prausnitz, J. M. *Am. Inst. Chem. Eng. J.* **1975**, *21*, 116.
(6) Renon, H.; Prausnitz, J. M. *Am. Inst. Chem. Eng. J.* **1968**, *14*, 135.
(7) Henley, E. J.; Seader, J. D. *Equilibrium-Stage Separation Operations in Chemical Engineering*; John Wiley & Sons: New York, 1981.
(8) Blanco, A.; Correa, J. M.; Arce, A.; Correa, A. *Can. J. Chem. Eng.* **1988**, *66*, 136.
(9) Roddy, J. W.; Coleman, C. F. *Ind. Eng. Chem. Fundam.* **1981**, *20*, 250.

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Solubility of Aromatic Hydrocarbons in Water and Sodium Chloride Solutions of Different Ionic Strengths: C_2-Substituted Benzenes

Dean F. Keeley,* Melanie A. Hoffpauir, and John R. Meriwether

Departments of Chemistry and Physics and The Acadiana Research Laboratory, University of Southwestern Louisiana, Lafayette, Louisiana 70504-4250

The solubilities of ethylbenzene and 1,2-, 1,3-, and 1,4-dimethylbenzene in aqueous sodium chloride solutions having ionic strengths ranging from 0 to 5.00 mol dm^{-3} have been determined at 298.15 K. The solubilities were determined by headspace analysis using a multiple-injection interrupted-flow (MIIF) technique. The values for the Henry's law constants and aqueous/vapor partition coefficients for the compounds in the solutions studied are also given. Correlations between the measured aqueous solubilities and molar volume, molecular surface areas, and a simple group contribution model are given. Extrapolation of the correlations is used to estimate the aqueous solubilities of the tri- and tetramethylbenzenes, which are liquids at 298.15 K.

Solubility data for organic compounds in aqueous solutions as a function of ionic strength is needed in the solution of many industrial and environmental problems. Recently, we have been studying the components of the connate water which makes up the geopressured reservoirs found along the Louisiana and Texas Gulf coast. These hot, brine reservoirs, a possible future energy source, are usually saturated with natural gas—mostly methane and other light alkanes. They also contain a spectrum of aromatic compounds that range from benzene to alkyl-substituted anthracenes. The concentration of these aromatic compounds has been found to be a dynamic variable of the production of some reservoirs (*1*). We have been attempting to construct models of the reservoir which are consistent with the aromatic compounds concentration dynamics. As part of this program we have measured the solubility of benzene and toluene in NaCl brines having ionic strengths of 0-5.00 mol dm^{-3} (*2*). We present here data on the solubility of ethylbenzene and 1,2-, 1,3-, and 1,4-dimethylbenzene in brines under similar conditions.

Determining solubilities of substances with appreciable vapor pressures can be complicated by the partition of such substances between the solvent and the free gas space above the solvent. A headspace analysis technique, developed earlier (*2*), was used for this study because of its ease of execution and because the technique, rather than being complicated by partition, utilizes it.

Experimental Section

Instrumentation. As in our earlier study, measurements were made using a Varian Model 3700 gas chromatograph equipped with a specially constructed headspace attachment (*3*).

Table I. Molar Solubilities (S), Henry's Law Constants (k), and Partition Coefficients (K_p) for Ethylbenzene in Water and Aqueous Sodium Chloride of Ionic Strength (μ) at 298.15 K

μ/ (mol dm^{-3})	S/ (10^{-3} mol dm^{-3})	k^a/ (10^9 Pa)	K_p^b
0	1.66 ± 0.04	4.24 ± 0.11	3.24 ± 0.08
1	1.01 ± 0.05	6.95 ± 0.35	1.98 ± 0.09
2	0.549 ± 0.023	12.7 ± 0.52	1.07 ± 0.05
3	0.387 ± 0.007	18.0 ± 0.27	0.755 ± 0.014
4	0.202 ± 0.007	28.7 ± 1.1	0.473 ± 0.018
5	0.148 ± 0.015	47.1 ± 4.8	0.289 ± 0.029

^{a} $p = kx$ where x = solute mole fraction and p = solute partial pressure in pascals. ^{b} $K_p = x/y$ where x and y = solute mole fraction in the solution and vapor, respectively.

Table II. Molar Solubilities (S), Henry's Law Constants (k), and Partition Coefficients (K_p) for 1,2-Dimethylbenzene in Water and Aqueous Sodium Chloride of Ionic Strength (μ) at 298.15 K

μ/ (mol dm^{-3})	S/ (10^{-3} mol dm^{-3})	k/ (10^9 Pa)	K_p
0	2.09 ± 0.05	2.39 ± 0.08	5.69 ± 0.16
1	1.17 ± 0.05	4.19 ± 0.19	3.28 ± 0.16
2	0.637 ± 0.004	7.67 ± 0.04	1.70 ± 0.01
3	0.419 ± 0.012	11.6 ± 0.39	1.18 ± 0.03
4	0.241 ± 0.030	20.5 ± 2.8	0.673 ± 0.096
5	0.121 ± 0.021	41.9 ± 4.8	0.341 ± 0.059

Materials. The aromatic compounds used in this study were analyzed by gas chromatography prior to use. One sample of 1,2-dimethylbenzene (Aldrich Gold Label, 99.8%), two samples of 1,3-dimethylbenzene (Baker, 99.60%; Aldrich, 99.8%), and two samples of 1,4-dimethylbenzene (Baker, 99.78%; Aldrich Gold Label, 99.83%) were used without further purification. Samples of 1,2-dimethylbenzene and ethylbenzene (Baker) were fractionally distilled to a purity of 99.80 and 99.40%, respectively, prior to use. Sodium chloride (Baker Analyzed Reagent Grade) was dried at 110 °C prior to use. The deionized water had a conductivity of $<10^{-6}$ (Ω cm)$^{-1}$ at 298.15 K.

Sample Preparation, Analytical Procedure, and Data Reduction. Solubilities are determined from computed values for the solute/solvent system at saturation. The technique employed obtains these values by extrapolation of data such as that shown in Figure 1. The upper curve was determined for samples containing only vapor while the lower is for samples containing solute, solvent, and vapor in the headspace above the liquid. In the latter case, vapor removal disturbs the equilibrium between the hydrocarbon in the vapor and in solution. A multiple-injection interrupted-flow gas chromatographic

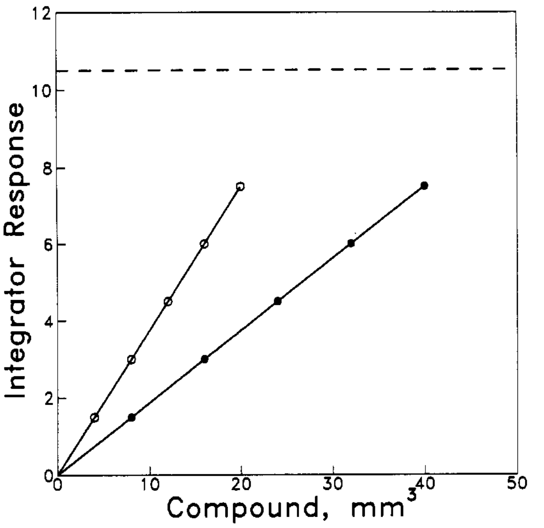

Figure 1. Typical "zero" flow time GC response as a function of mm^3 of hydrocarbon in the system: (○) vapor-only samples; (●) liquid-containing samples. The dashed line corresponds to the computed response at system saturation.

Table III. Molar Solubilities (S), Henry's Law Constants (k), and Partition Coefficients (K_p) for 1,3-Dimethylbenzene in Water and Aqueous Sodium Chloride of Ionic Strength (μ) at 298.15 K

μ/ (mol dm^{-3})	S/ (10^{-3} mol dm^{-3})	k/ (10^9 Pa)	K_p
0	1.58 ± 0.02	3.89 ± 0.04	3.53 ± 0.04
1	0.923 ± 0.032	6.64 ± 0.23	2.06 ± 0.07
2	0.567 ± 0.011	10.8 ± 0.20	1.27 ± 0.03
3	0.294 ± 0.015	20.7 ± 1.2	0.659 ± 0.033
4	0.179 ± 0.007	33.9 ± 1.2	0.401 ± 0.015
5	0.0957 ± 0.0021	62.9 ± 1.3	0.214 ± 0.005

Table IV. Molar Solubilities (S), Henry's Law Constants (k), and Partition Coefficients (K_p) for 1,4-Dimethylbenzene in Water and Aqueous Sodium Chloride of Ionic Strength (μ) at 298.15 K

μ/ (mol dm^{-3})	S/ (10^{-3} mol dm^{-3})	k/ (10^9 Pa)	K_p
0	1.63 ± 0.02	3.97 ± 0.05	3.46 ± 0.05
1	0.846 ± 0.019	7.63 ± 0.17	1.79 ± 0.04
2	0.512 ± 0.010	12.6 ± 0.25	1.09 ± 0.02
3	0.288 ± 0.006	22.4 ± 0.40	0.611 ± 0.012
4	0.152 ± 0.005	42.1 ± 1.5	0.322 ± 0.011
5	0.109 ± 0.015	60.8 ± 4.7	0.223 ± 0.017

technique (MIIF), an extension of the work of Massaldi and King (*4*), was developed in which a series of vapor aliquots were taken at known flow times and a linear extrapolation of their GC responses made to obtain the GC response at equilibrium. Details of the sample preparation, analytical procedure, and data reduction are given in ref 2.

Results. Solubilities, Henry's law constants, and aqueous/vapor partition coefficients for ethylbenzene and 1,2-, 1,3-, and 1,4-dimethylbenzene are given in Tables I–IV, respectively, for aqueous NaCl solutions with ionic strength μ = 0–5.00 mol dm^{-3}.

Discussion

In Figure 2 we have plotted the solubilities for benzene and toluene from our earlier work (*2*) and the solubilities for the C$_2$-substituted benzenes from this study as a function of the molar volumes listed in Table V. The linear correlation coefficients of the Figure 2 plots at ionic strength μ = 0–5 mol dm^{-3} are 0.999, 0.998, 1.000, 0.997, 0.997, and 0.992, respectively. While such plots are popular, they suffer from the objection that while molar volumes computed from solute densities and molecular weights may be proportional to the effective volume of solute molecules in the pure solutes, they are not necessarily true indicators of the effective volumes of solute molecules in other solvents.

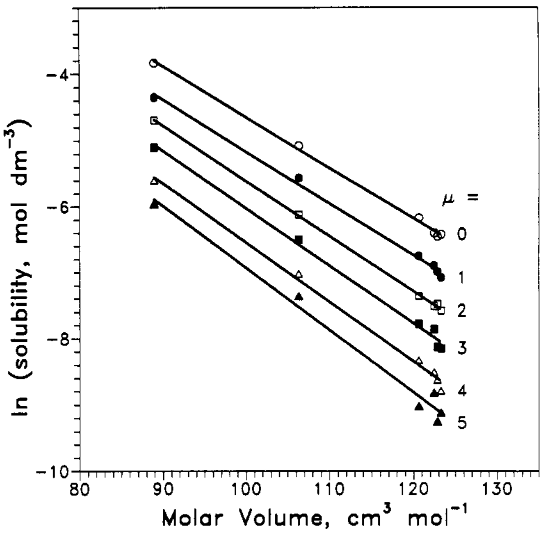

Figure 2. Logarithm of the aqueous solubility of benzene, methylbenzene, ethylbenzene, and 1,2-, 1,3-, and 1,4-dimethylbenzene as a function of molar volume and ionic strength (μ) at 298.15 K.

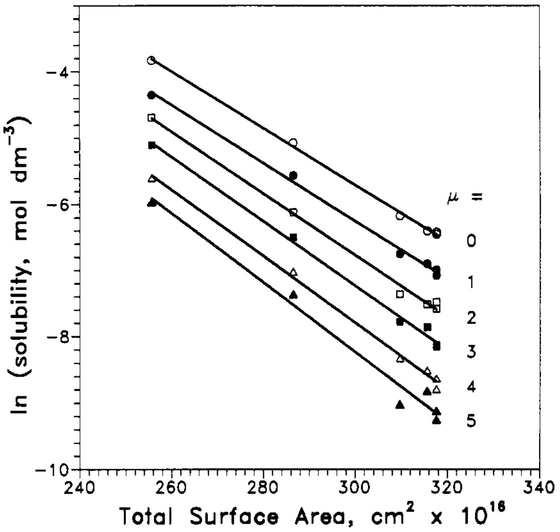

Figure 3. Logarithm of the aqueous solubility of benzene, methylbenzene, ethylbenzene, and 1,2-, 1,3-, and 1,4-dimethylbenzene as a function of molecular surface area and ionic strength (μ) at 298.15 K.

Table V. Molar Volumes (V) and Molecular Surface Areas (A)

compound	V/(cm^3 mol^{-1})	A/(10^{-16} cm^2)
benzene	88.91	255.7
methylbenzene	106.3	286.5
ethylbenzene	122.5	315.6
1,2-dimethylbenzene	120.6	309.7
1,3-dimethylbenzene	122.9	317.6
1,4-dimethylbenzene	123.3	317.6

More recently the use of molar volume has been replaced by molecular surface area (MSA), originally suggested by Langmuir (*19*) in connection with solution free energies, as a more appropriate variable. While molecular surface areas are theoretically more appealing, they are not easily computed. Figure 3 is a plot of solubility values from this study as a function of MSA. The MSA values used, Table V, are those of Amidon et al. (*20*). Linear correlation coefficients for the Figure 3 plots for ionic strength μ = 0–5 mol dm^{-3} are 0.999, 0.998, 0.998,

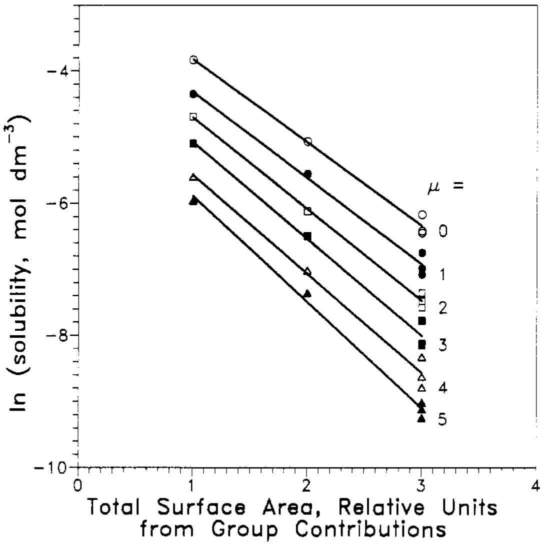

Figure 4. Logarithm of the aqueous solubility (S) of benzene, methylbenzene, and 1,2-, 1,3-, and 1,4-dimethylbenzene as a function of group contributions and ionic strength at 298.15 K. For the aqueous line: ln (S/(mol dm^{-3})) = $-1.26\sum GC = 2.56$, where $\sum GC = 1$, 2, and 3 for benzene, methylbenzene, and the dimethylbenzenes, respectively.

0.998, and 0.990, respectively.

Benzene and its C_1- and C_2-substituted analogues are all liquids at room temperature. With the exception of ethylbenzene, these substances may be viewed as rigid molecules in which a benzene hydrogen has been replaced by a methyl group. To a first approximation, the molecular volumes (MV) or molecular surface areas (MSA) of such a series can be represented by a sum of group contributions

$$\sum GC = B = nH_B + n(M - H_M) \qquad (1)$$

where n is the number of methyl groups, B is the benzene value and M the methane values for the appropriate property, and H_B and H_M are the corrections to the value corresponding to the removal of one hydrogen atom from benzene and methane, respectively.

Equation 1 may be simplified to

$$\sum GC = B + nS \qquad (2)$$

where $S = M - H_B - H_M$. Figure 4 is a plot of the natural logarithms of the aqueous solubilities of benzene, toluene, and 1,2-, 1,3-, and 1,4-dimethylbenzene as a function of their $\sum GC$ values as computed from eq 2 in which B and S have been assigned arbitrary values of 1 and for which $n = 0$, 1, and 2 for benzene, methylbenzene, and the dimethylbenzenes, respectively. The linear correlation coefficients of the aqueous solubility data plotted in this fashion are, for $\mu = 0$–5 mol dm^{-3}, 0.995, 0.994, 0.998, 0.994, 0.992, and 0.997, respectively. Since such plots find their greatest use in estimating solubilities, the authors feel that when conditions and available data justify it, a simple approach like eq 2 gives a useful first approximation.

Table VI contains estimated values for the aqueous solubilities of the tri- and tetramethylbenzenes, which are liquid at 298.15 K, based on an extrapolation of the data in Figures 2–4. Literature values, where available, are also given for comparison.

Tables VII and VIII list published solubilities and Henry's law constants, respectively, for ethylbenzene and 1,2-, 1,3-, and 1,4-dimethylbenzene. The range of values, obtained by capable investigators using a variety of methods, attest to the difficulty associated with measuring aqueous solubilities of slightly soluble organic compounds that have appreciable vapor pressures. The primary difficulty encountered is the rapid desorption of these compounds from aqueous solutions, which we have observed during multiple-injection headspace analysis (*2*). As a consequence of this rapid desorption, physical manipulation of the solutions must either be avoided completely or done with great care so as to either avoid or compensate for solute loss. Indeed, any analytical procedures for determining the aqueous concentrations of such compounds which employ physical manipulations, such as open pouring, of the aqueous solution are inherently flawed.

Table VI. Literature Values and Estimated Aqueous Solubilities (S) of Tri- and Tetramethylbenzenes at 298.15 K from Extrapolation of Least-Squares Fit from Figures 2–4

	$S/(10^{-3}$ mol dm$^{-3})$				
	tri-methylbenzenes			tetra-methylbenzenes	
	1,2,3-	1,2,4-	1,3,5-	1,2,3,4-	1,2,3,5-
molar volume	0.833	0.587	0.417	0.238	0.197
MSA	0.688	0.557	0.487		
from eq 2	0.500	0.500	0.500	0.142	0.142
	Literature Values				
ref 9	0.520	0.469	0.415	NA	NA
ref 11	0.626	0.491	0.401		
ref 10		0.47			
ref 13		0.432			
ref 18	0.545				
mean	0.564	0.466	0.408		
std dev	±0.055	±0.025	±0.010		

Table VII. Solubilities (S) in Water at 298.15 K from This Work Compared to Other Sources

solute	$S/(10^{-3}$ mol dm$^{3})$	
ethylbenzene	1.66 (this work)	1.43 (*10*)
	2.00 (*5*)	1.518 (*11*)
	1.96 (*6*)	1.58 (*12*)
	1.74 (*7*)	1.23 (*13*)
	1.67 (*8*)	1.3 (*14*)
	1.59 (*9*)	1.64 (*15*)
	1.55 (*16*)	1.76 (*18*)
1,2-dimethylbenzene	2.09 (this work)	1.57 (*13*)
	2.01 (*8*)	1.63 (*12*)
	1.68 (*9*)	1.606 (*11*)
	1.65 (*10*)	2.08 (*18*)
1,3-dimethylbenzene	1.58 (this work)	1.85 (*6*)
	1.53 (*8*)	1.375 (*11*)
	1.45 (*9*)	1.26 (*13*)
	1.48 (*17*)	1.51 (*18*)
1,4-dimethylbenzene	1.63 (this work)	1.86 (*6*)
	1.74 (*8*)	1.48 (*13*)
	1.50 (*9*)	1.469 (*11*)
	1.88 (*12*)	1.54 (*17*)
	2.02 (*18*)	

Table VIII. Henry's Law Constant (k) for the Solute in Water at 298.15 K from This Work Compared to Other Sources

solute	$k/(10^9$ Pa)	
ethylbenzene	4.24 (this work)	4.43 (*9*)
		3.59 (*6*)
1,2-dimethylbenzene	2.39 (this work)	2.92 (*9*)
1,3-dimethylbenzene	3.89 (this work)	4.07 (*9*)
		3.32 (*6*)
1,4-dimethylbenzene	3.97 (this work)	4.24 (*9*)
		3.48 (*6*)

Conclusions

This and our previous study have shown the MIIF headspace analysis technique to be a simple, sensitive, and accurate method for determining solubilities, Henry's law constants, and partition coefficients of nonelectrolytes that have appreciable vapor pressures. With this study, the solubilities of benzene and its C_1- and C_2-substituted analogues have been determined by a single method in water and in aqueous NaCl solutions having ionic strengths μ = 0-5 mol dm^{-3}. These solubilities will be useful in estimating environmental impacts and in other industrial problems. When it is applicable, and in the absence of data needed by more sophisticated techniques, eq 2 offers a way to at least estimate the solubilities. Indeed for 1,2,3- and 1,2,4-trimethylbenzene, the solubilities estimated from eq 2 and Figure 4 are in better agreement with mean literature solubility values than are the values predicted from the extrapolation of either the molar volume, Figure 2, or molecular surface area, Figure 3, plots.

Literature Cited

(1) Keeley, D. F.; Meriwether, J. R. *J. Energy Resour. Technol.* **1988**, *110*, 177.
(2) Keeley, D. F.; Hoffpauir, M. A.; Meriwether, J. R. *J. Chem. Eng. Data* **1988**, *33*, 87.
(3) Keeley, D. F.; Meriwether, J. R. *Rev. Sci. Instrum.* **1986**, *57*, 1434.
(4) Massaldi, H. A.; King, C. J. *J. Chem. Eng. Data* **1973**, *18*, 393.
(5) Ben-Naim, A.; Wilf, J. *J. Phys. Chem.* **1980**, *84*, 583.
(6) Bohon, R. L.; Clausen, W. F. *J. Am. Chem. Soc.* **1951**, *73*, 1571.
(7) Owens, J. W.; Wasik, S. P.; Devoe, H. *J. Chem. Eng. Data* **1986**, *31*, 47.
(8) Polak, J.; Lu, B. C. Y. *Can. J. Chem.* **1973**, *51*, 4018.
(9) Sanemasa, I.; Araki, M.; Deguichi, T.; Nagai, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1054.
(10) McAuliffe, C. *J. Phys. Chem.* **1966**, *70*, 1267.
(11) Sutton, C.; Calder, J. A. *J. Chem. Eng. Data* **1975**, *20*, 320.
(12) Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1950**, *72*, 5034.
(13) Price, L. C. *Am. Assoc. Pet. Geol. Bull.* **1976**, *60*, 213.
(14) Fuhner, H. *Chem. Ber.* **1924**, *57*, 510.
(15) Klevens, H. B. *J. Phys. Colloid Chem.* **1950**, *54*, 283.
(16) Morrison, T. J.; Billett, F. J. *J. Am. Chem. Soc.* **1952**, *74*, 3819.
(17) Hermann, R. B. *J. Phys. Chem.* **1972**, *76*, 2754.
(18) Tewari, Y. B.; Miller, M. M.; Wasik, S. P.; Martire, D. E. *J. Chem. Eng. Data* **1982**, *27*, 451.
(19) Langmuir, I. *Third Colloid Symposium Monograph*; Chemical Catalog Co.: New York, 1925; p 3.
(20) Amidon, G. L.; Anik, S. T. *J. Chem. Eng. Data* **1981**, *26*, 28.

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Solubility and Diffusivity of Oxygen and Chlorine in Aqueous Hydrogen Peroxide Solutions

Gabriel Ruiz-Ibanez, Ali Bidarian, Richard A. Davis, and Orville C. Sandall*

Department of Chemical & Nuclear Engineering, University of California, Santa Barbara, California 93106

In this work the solubility and diffusion coefficients of oxygen in aqueous hydrogen peroxide solutions have been measured. The solubility of chlorine in 0.1 N HCl and 1 N KCl/0.1 N HCl solutions was measured along with the diffusivity of chlorine in aqueous hydrogen peroxide solutions. The measurements were conducted over the temperature range +20 to −10 °C. Methods are proposed to use the measurements of this work in order to predict the solubility and diffusivity of these gases in an aqueous solution of basic hydrogen peroxide.

Considerable interest has recently been shown in singlet delta oxygen [$O_2(^1\Delta_g)$], which is molecular oxygen in its lowest excited electronic state (*1*). This is mainly due to its use in the chemical oxygen-iodine laser (COIL) in which metastable $O_2(^1\Delta_g)$ pumps iodine to an electronically excited atomic state that lases as the iodine atoms release their energy (*2*). The performance of a COIL depends on the ability to produce $O_2(^1\Delta_g)$ generated from its singlet oxygen generator.

The chemical reaction between chlorine and basic hydrogen peroxide (BHP) is the most common reaction used for the production of singlet oxygen. The stoichiometry of this reaction is as follows:

$$2KOH + H_2O_2 + Cl_2 \rightarrow 2KCl + 2H_2O + O_2(^1\Delta_g) \quad (1)$$

In order to interpret kinetic studies of this reaction and for reactor design, it is necessary to have knowledge of the solubility and diffusivity of chlorine and oxygen in BHP solutions. It is the solubility of the unreacted gas in the case of Cl_2 and not the total solubility that is of interest here. It is not possible to directly measure these physicochemical properties in BHP solutions. This is due to the fact that Cl_2 reacts with fast kinetics in BHP and that these solutions are quite unstable, with H_2O_2 decomposing to H_2O and O_2. In the work reported here, we have measured O_2 and Cl_2 solubilities and diffusivities in aqueous hydrogen peroxide solutions over a range of temperatures and propose methods to extrapolate these measurements in order to predict these properties in BHP solutions.

A gas/liquid solubility apparatus which volumetrically measures the volume of gas dissolved in a known volume of liquid was used to measure the solubilities. A laminar liquid jet absorber was used to measure the diffusivity of Cl_2 and a wetted-sphere absorber was used to measure the diffusivity of O_2.

Experimental Equipment

Solubility Apparatus. This apparatus is used to measure the solubility of a gas in a liquid solution. The principle idea of the method used here is to bring a known volume of liquid into contact with a volume of gas in a closed system at constant temperature and pressure. Equilibrium is reached by agitating the liquid for some time until no change in the volume of the gas is observed. The amount of gas absorbed is measured volumetrically. This apparatus, shown in Figure 1, was modified from the original solubility apparatus described by Haimour and Sandall (*3*). The main modification for this work was the addition of a spherical volume in the mercury buret. The sphere, which has a volume of 48.2 mL, allows a larger volume of liquid sample to be injected into the equilibrium cell and thereby increases the volume of gas absorbed at equilibrium. This modification was necessary for the experiments with oxygen because of its relatively low solubility.

Figure 1 also shows a further modification of the solubility apparatus that was made for measurements using chlorine. The Cl_2 reacted with mercury and several substitute manometer fluids, such as butyl phthalate, silicon oil, Meriam red and blue oil (brominated aromatics), and aqueous hydrochloric acid solutions. The solution to this problem was to include two coils in the gas lines, as shown in Figure 1. One coil, labeled I, which initially contains air, delays the diffusion of chlorine to the

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