Solubility Data on Chlorine in Monochlorobenzene and Hydrogen Chloride in 1-Octanol and 1-Dodecanol

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Equilibrium solubilities for chlorine in monochlorobenzene are reported for the temperature range 30° to 60° C. and for hydrogen chloride in 1-octanol and 1-dodecanol for the range 57° to 132° C. for solute partial pressures of 1 atm.

IN SOME studies of reaction kinetics (*2, 5*) in heterogeneous chlorination and hydrochlorination systems the solubility of reactant gas in the liquid phase reactant was determined. Such data are reported here for three systems: chlorine-monochlorobenzene at 30° to 60° C., hydrogen chloride–1-octanol at 57° to 131° C., and hydrogen chloride–1-dodecanol at 65° to 132° C. The measurements are all for solute partial pressures of 1 atm. and the temperature ranges correspond to solubilities in the general range of 0.5 to 3.5 gram moles per liter.

EXPERIMENTAL

The monochlorobenzene employed in this work was Fisher Scientific certified reagent. Analysis: water, 0.0%; nonvolatile matter, 0.01%. First, 1.5 liters of the material were distilled over calcium hydride. The first 300 ml. of distillate were discarded and the next 900 ml. collected over calcium hydride, stored in the dark, and subsequently used in experimentation. The 1-octanol and 1-dodecanol supplied were Matheson, Coleman and Bell research grade, whose purity was determined as 98.5 and 97.5 mole %, respectively, by chromatographic analysis (*2*). Purification by distillation was carried out by collecting the middle distillate fraction (250 ml.) of a 750-ml. charge; purities of this fraction were 99.3 and 99.8%, respectively, and this was employed in the experimentation. In both cases the impurities were due to the presence of lower alcohols: butanol and hexanol in the 1-octanol and octanol and decanol in the 1-dodecanol.

The gases used were supplied by the Matheson Co.: high purity grade chlorine ($99.5^+\%$ Cl_2), dried by passage through concentrated sulfuric acid, and electronic grade hydrogen chloride (99.99% minimum HCl).

Chlorine solubilities in monochlorobenzene were determined as follows. A given amount, normally 150 ml., of monochlorobenzene was saturated with chlorine at 10° C. by bubbling the gas through the liquid until the concentration of dissolved chlorine, determined by the iodometric technique of LePage and Jungers (*4*), was constant over a half-hour period. The temperature of the solution was then raised to the desired level and the chlorine concentration again allowed to equilibrate. At this point, 2 ml. of a solution of $SnCl_4$ dissolved in chlorobenzene (about 0.5 gram mole per liter of $SnCl_4$) was added to the chlorine-saturated solution. Under the conditions of experimentation the chlorination of monochlorobenzene is irreversible (*4*), and the reaction was allowed to proceed at the set temperature to completion after the addition of catalyst—i.e., total consumption of chlorine. Blank tests conducted over the same temperature range indicated that chlorine evolution from the samples for time periods corresponding to reaction times was less than 1% of the total even at the highest concentrations. The solubility, then, was calculated from the conversion to dichlorobenzene as measured by a chromatographic method (*5*) with correction for the unsaturated catalyst solution added. The use of this reaction technique rather than direct analysis of chlorine concentration (although this latter was used as a guide for composition equilibration) avoided some rather troublesome problems with reproducibility because of difficulties in keeping the chlorine in solution during titration.

Hydrogen chloride solubilities in the two alcohols were determined more straightforwardly by direct sampling and analysis, since evolution of dissolved gas could be suppressed in these systems. Samples were saturated at the lowest temperature reported (57° C. for 1-octanol and 65° C. for 1-dodecanol), the condition of saturation being defined when consecutive analyses for HCl concentration over a half-hour period did not vary. Solubilities at higher temperatures were determined by heating such solutions to the desired temperatures and following a similar procedure of sampling and analysis. Hydrogen chloride concentration was determined by titrating against a standardized sodium hydroxide solution with phenolphthalein as the indicator. The evolution of hydrogen chloride during titration was prevented by very slow addition of the sodium hydroxide solution.

The accuracy of the measured solubilities in both cases is felt to be limited by the accuracy of analytical methods. Random errors in volume determinations are on the order of ±0.05 ml., and temperature uncertainty is likewise on the order of ±0.05° C. The sodium hydroxide concentration is known to 1%; this concentration uncertainty plus volumetric errors limits the accuracy of the hydrogen chloride titration to (conservatively) ±3% of reported values (*2*). Accuracy of the chromatographic analysis for dichlorobenzene is limited by the reproducibility of the machine calibration, which was ±1% (*5*). This, again, leads to a conservative estimate of ±3% variation for reported

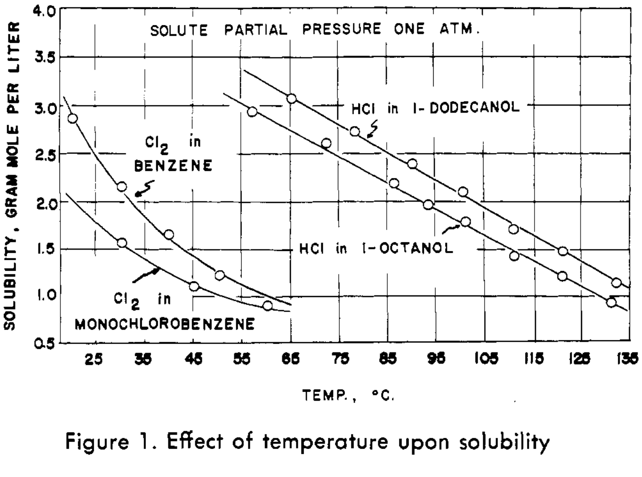

Figure 1. Effect of temperature upon solubility

solubility values. Complete experimental details are given by Silberstein (*5*) and Daté (*2*).

RESULTS

The solubilities measured for the three systems are given in Figure 1 as a function of temperature, together with the data of Krivonos (*3*) for chlorine in benzene as a reference for the chlorine-monochlorobenzene system. Krivonos showed that semilogarithmic plots of solubility *vs.* temperature are linear for a number of chlorine systems and the present data for monochlorobenzene are in accord with this, so relatively reliable temperature extrapolation is possible. The strong temperature-dependence in this case is probably due to the influence of molecular association complexes (*1*) between chlorine and these solvents. Solubilities of hydrogen chloride in the two alcohols are essentially linear in temperature over the range investigated, and extrapolation to higher temperatures is certainly possible. Numerical values for the measured solubilities and the corresponding Henry's law constants are reported in Table I.

Table I. Solubilities and Henry's Law Constants

System	Temp., °C.	Solubility, G. Moles/Liter	Henry's Law Constant[a], Atm.-Liter/G. Mole
Cl_2-C_6H_6	10.0	3.97	0.252
	20.0	2.86	0.350
	30.0	2.14	0.468
	40.0	1.65	0.607
	50.0	1.20	0.834
Cl_2-C_6H_5Cl	30.0	1.56	0.641
	45.0	1.10	0.909
	60.0	0.78	1.282
HCl-$C_8H_{17}OH$	57.0	2.93	0.341
	72.0	2.61	0.383
	86.0	2.18	0.459
	93.5	1.97	0.508
	101.0	1.79	0.559
	111.0	1.41	0.710
	121.0	1.19	0.841
	131.0	0.93	1.075
HCl-$C_{12}H_{25}OH$	65.0	3.06	0.327
	78.0	2.73	0.366
	90.1	2.39	0.418
	100.5	2.09	0.478
	111.0	1.71	0.585
	121.0	1.47	0.680
	132.0	1.13	0.885

[a] Henry's law constant defined as $H \equiv P/C$, where P is partial pressure of solute in atmospheres and C is corresponding equilibrium solubility.

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Thermal Conductivity of Phosphoric Acid

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The thermal conductivity of phosphoric acid was measured in glass cells calibrated with water and with aqueous solutions of glycerol and of sulfuric acid. The results were expressed with an average deviation of 1.7% by the equation: $K \times 10^4 = 11.727 + 0.01864T - 0.02169C - 0.0000338CT$, in which K is thermal conductivity, cal./(cm.)(sec.)(° C.); T is temperature, ° C., 25° to 150°; and C is concentration, weight % H_3PO_4, 84 to 115% (61 to 83% P_2O_5).

THE GROWING use of concentrated phosphoric acid, especially in the manufacture of ammonium polyphosphate fertilizers, has increased the need for information on its properties. Turnbull (*9*) recently reported thermal conductivity data on phosphoric acid but did not cover the desired high temperatures and concentrations. This report covers measurements of the thermal conductivity of phosphoric acid over the concentration range 84 to 115% H_3PO_4 (61 to 83% P_2O_5) and the temperature range 25° to 150° C. The results are expressed in a single equation.

MATERIALS AND APPARATUS

Thermal conductivity measurements were made on acid produced in the TVA demonstration plant (*1*) that contained 114% H_3PO_4 and on its solutions diluted to 111, 97, 91, and 84% H_3PO_4. Each diluted solution was heated sufficiently to equilibrate the phosphate species. Three other solutions containing 115, 101, and 86% H_3PO_4 were prepared by dissolving reagent P_4O_{10} in reagent (85%) H_3PO_4. The concentrations of the phosphoric acid solutions were determined by the gravimetric quinoline molybdate method for phosphorus (*2*) with an accuracy of about 0.1% at the highest concentrations. The glycerol and sulfuric acid were reagent grade, and the concentrations of their solutions were determined by Karl Fischer and alkalimetric titrations, respectively.

Turnbull (*9*) measured thermal conductivities of phosphoric acid solutions in a hot-wire apparatus, but attempts to repeat his work were unsuccessful. Although Turnbull