Solubility of Hydrogen in Chlorobenzene

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Reliable data on the solubility of molecular hydrogen in chlorobenzene have been collected at temperatures from 273.2 to 443.2 K and pressures to 65 bar. Henry's constant rendered from a preliminary analysis of the data is reported as a function of temperature. The influence of dissolved acrylonitrile−butadiene copolymer on the solubility has been established for 4.09 and 8.08 mass % solutions.

Introduction

The hydrogen + chlorobenzene system is relevant to the commercial synthesis of modified butadiene copolymers. Derived from traditional elastomers, this new class of specialty rubbers has largely fulfilled market demands for improved chemical and thermal resistance. A leading example is hydrogenated acrylonitrile−butadiene copolymer, currently produced by Bayer Rubber through the catalytic hydrogenation of nitrile−butadiene rubber (NBR) (Oppelt et al., 1976). The suitability of chlorobenzene as an inert solvent for the copolymer has led to its adoption for the industrial hydrogenation process. The rapid development of the hydrogenated NBR (HNBR) market has led to further research into processes of this kind, creating a need for reliable estimates of the solubility of hydrogen in chlorobenzene at industrial conditions. However, the only report on this system is limited to 1.013 bar over a temperature range of 232.3−354.0 K (Horiuti, 1931).

In the present paper, the solubility of hydrogen in pure chlorobenzene and dilute NBR solutions is measured at temperatures ranging from 273.2−443.2 K and total pressures up to 65 bar. These conditions encompass those commonly encountered by catalyst researchers and process designers working in the polymer modification field (McManus and Rempel, 1995).

Experimental Section

Materials. All reagents were used as received. Hydrogen gas of 99.99% purity was obtained from Linde-Union Carbide Canada Ltd. The chlorobenzene purchased from Fisher Scientific Ltd. had a reported purity of 99%. All other solvents were spectrometric grade products of Aldrich Chemical Co. Samples of nitrile−butadiene rubber with a number average molecular weight of 200 000 were obtained from Bayer Rubber Inc.

Apparatus and Procedure. A high-pressure autoclave with an internal volume of 600 cm^3 was used to prepare samples of H_2 + chlorobenzene. Equilibrium was established rapidly using a high-velocity impeller to intimately mix the vapor and condensed phases. In general, 30 min was found to be sufficient following a change in pressure while at least a 90 min equilibration time was observed after changing temperatures. The results obtained were unaffected by approaching the experimental pressure from above or below.

Of the 350 cm^3 of chlorobenzene initially charged to the autoclave, no more than 250 cm^3 was withdrawn for analysis before recharging. In each case, the system was degassed using three cycles of charging the reactor with H_2 to 10 bar, allowing the system to equilibrate under vigorous agitation, and then releasing the pressure. The total system pressure was measured by a differential pressure transducer that was calibrated to an estimated accuracy of ±1% of the range studied, or ±65 kPa at 65 bar. An iron−constantan thermocouple, checked at the ice and steam points, was used to measure the temperature of the condensed phase. Control of the vessel temperature was accomplished to within ±0.5 K by a PID controller acting on a ceramic insulated heating mantle.

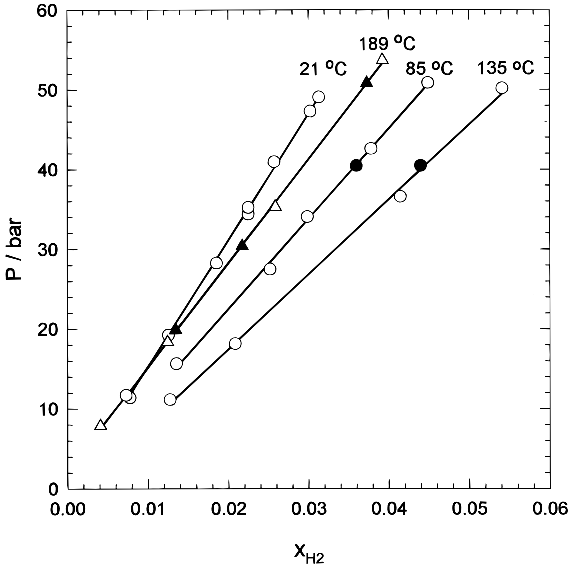

Figure 1. Comparison of the developed technique to published work: △, *m*-xylene; ○, *n*-decane; ▲, Simnick et al.; ●, Sokolov and Polyakov.

The analysis technique, based on the work of Lee and Mather (1977), focused solely on the composition of the condensed phase. Samples were withdrawn from the autoclave through a 1.59 mm o.d. dip tube which was purged of any vapor. Approximately 15 cm^3 of liquid was collected into a stoppered, 125 cm^3 sample flask. Once brought to room temperature, the volume of H_2 evolved from the sample was measured using a mercury leveled gas buret. The buret system was filled with pure hydrogen at atmospheric pressure prior to each measurement. A correction for residual H_2 dissolved in the liquid was applied while the vapor prssure of the solvent was considered negligible. The amount of chlorobenzene sampled in the procedure was then measured gravimetrically. In those studies where copolymer solutions were studied, the composition of the liquid was determined by evaporation of the solvent and weighing the polymer residue.

Results

To verify that the experimental method was capable of yielding results of an accuracy sufficient for practical

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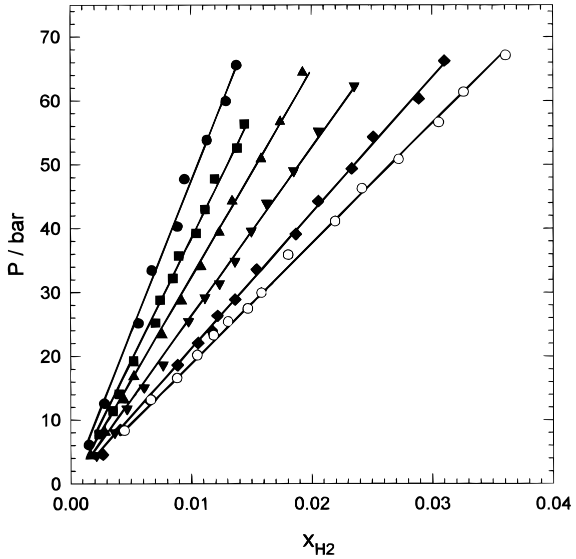

Figure 2. Solubility of H_2 in chlorobenzene: ●, 0 °C; ■, 23 °C; ▲, 55 °C, ▼, 90 °C; ◆, 130 °C, ○, 170 °C.

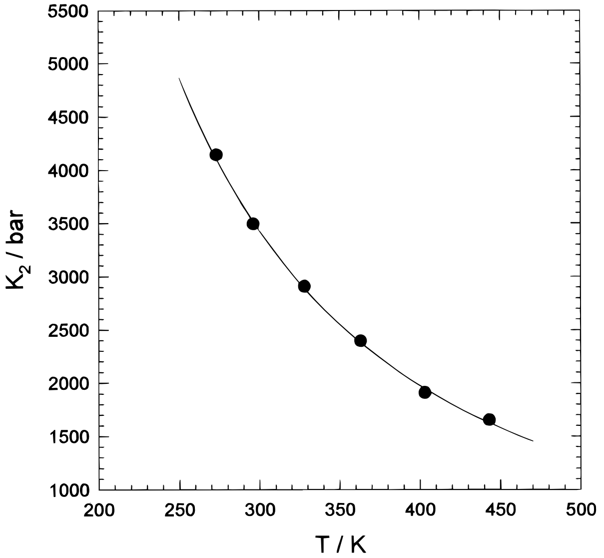

Figure 3. K_2 verses temperature for H_2 + chlorobenzene: ●, experimental; —, least squares regression.

Table 1. Solublity of H_2 in Chlorobenzene

$T = 273.2$ K		$T = 296.2$ K		$T = 328.2$ K	
P/bar	$10^2 x$H$_2$	P/bar	$10^2 x$H$_2$	P/bar	$10^2 x$H$_2$
6.1	0.15	14.1	0.40	13.2	0.44
25.1	0.56	19.2	0.52	23.3	0.76
33.4	0.67	25.2	0.70	28.6	0.92
40.3	0.89	28.8	0.74	34.1	1.08
47.7	0.94	32.2	0.85	39.4	1.23
53.8	1.13	35.7	0.90	44.3	1.34
59.9	1.29	39.2	1.04	50.9	1.58
65.6	1.38	43.0	1.11	56.7	1.74
		47.8	1.19	64.4	1.93
		52.5	1.38		
		56.3	1.44		

$T = 363.2$ K		$T = 403.2$ K		$T = 443.2$ K	
P/bar	$10^2 x$H$_2$	P/bar	$10^2 x$H$_2$	P/bar	$0^2 x$H$_2$
11.7	0.47	8.4	0.41	13.2	0.66
15.1	0.61	13.1	0.72	16.5	0.88
18.6	0.77	18.6	0.89	20.1	1.05
25.4	0.98	22.1	1.06	23.2	1.19
29.2	1.13	24.0	1.17	25.4	1.31
31.4	1.23	26.3	1.22	27.4	1.47
34.9	1.36	28.9	1.36	29.9	1.58
39.6	1.50	33.6	1.54	35.9	1.81
44.0	1.62	39.1	1.87	41.1	2.20
49.0	1.85	44.3	2.06	46.3	2.42
55.2	2.06	49.4	2.34	50.8	2.72
62.3	2.36	54.3	2.51	56.6	3.06
		60.3	2.89	61.4	3.26
		66.3	3.10	67.1	3.61

applications, a comparison with published solubility data was made. Two reports, produced by separate laboratories, were selected for comparison over the range of conditions relevant to HNBR production. The first, reported by Sokolov and Polyakov (1977), examined the hydrogen + *n*-decane system. The second comparison was made with the work of Simnick et al. (1979) on the hydrogen + 1,3-dimethylbenzene system. Figure 1 illustrates both the literature studies along with the data collected in our laboratory using the procedure described above. In no case did the deviation of the literature data from the values calculated from a linear regression of our results exceed 2%. In a review of the work of Sokolov and Polyakov, Young (1981) assigned an error of ±3% to the reported H_2 liquid mole fraction. In light of our comparison to the work, this error estimate is considered to be representative of that associated with the present study.

Having established confidence in the experimental approach, the H_2 + chlorobenzene system was analyzed at 273.2, 296.2, 328.2, 363.2, 403.2, and 443.2 K at pressures up to 65 bar. Figure 2 illustrates the liquid phase H_2 mole fraction as a function of the system conditions while numerical values are provided in Table 1. Owing to the lack of vapor phase data, any analysis must be classified as preliminary. Nevertheless, the data appear to be well represented by eq 1 over the range of conditions studied. Defined by eq 1, K_2 (at the saturation pressure of chlorobenzene) is the limiting value of f_2/x_2 as the system approaches infinite dilution.

$$\ln(f_2/x_2) = \ln K_2 + (v_{m,2}/RT)P_{H_2} \qquad (1)$$

f_2 = fugacity of H_2, bar

x_2 = H_2 liquid mole fraction

K_2 = Henry's constant, bar

$v_{m,2}$ = liquid molar volume of H_2, m^3/mol

T = system temperature, K

P_{H2} = partial pressure of H_2, bar

Without a knowledge of the vapor phase composition, certain simplifications are necessary in order to estimate the fugacity of hydrogen, f_2. The first assumption is that Raoult's law may be applied to estimate the vapor phase hydrogen mole fraction. The second assumes that a binary interaction between H_2 and chlorobenzene may be neglected. This last simplification facilitates an estimate of the vapor phase fugacity coefficient for H_2 from the equation of state of Peng and Robinson (1976). Through these assumptions, Henry's constant at each temperature has been regressed and plotted in Figure 3. The overall temperature dependence of K_2 has been fitted to the expression provided in eq 2 using the units specified above.

$$\ln K_2^{P_1^{\text{sat}}} = 19.061 + 0.483/T - 1.915 \ln T \qquad (2)$$

A comparison of eq 2 with a correlation reported by Fogg and Gerrard (1991) of the data of Horiuti (1931) is favorable. Over the coincident temperature range (273–354 K), the largest deviation between predicted values is 9.1%.

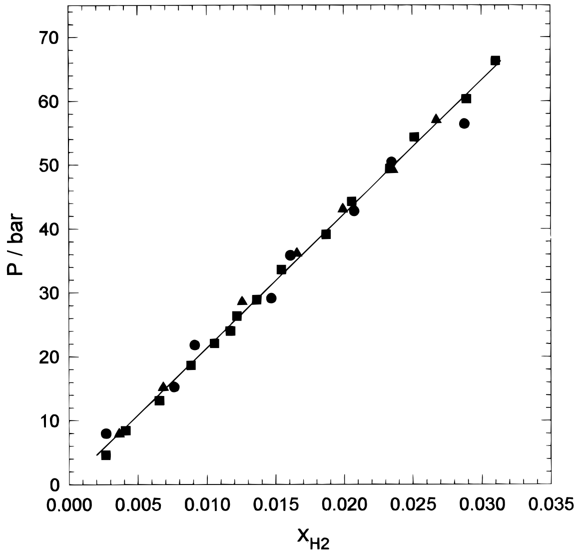

Figure 4. Solubility of H_2 in NBR + chorobenzene solutions, T = 303.2 K: ■, pure chlorobenzene; ●, 4.09 mass % NBR; ▲, 8.08 mass % NBR.

As the utility of the H_2 + chlorobenzene system lies principally with the hydrogenation of copolymers, the influence of dissolved polymer on the hydrogen solubility is required for practical application of the data. Therefore, solutions of 4.09 and 8.08 mass % NBR in chlorobenzene have been analyzed for comparison to pure solvent data. Figure 4 suggests that at the relatively low copolymer loadings studied, the influence of NBR on the H_2 solubility is not significant. In addition, fluid densities at room temperature for both polymer solutions were indistinguishable within engineering tolerances.

Conclusions

The hydrogen + chlorobenzene system adheres to a Henry's law assumption over the temperature range of 273.2−443.2 K and pressures up to 65 bar. Estimates of Henry's constant as a function of temperature may be effectively represented by a three-parameter regression. The influence of dissolved acrylonitrile−butadiene copolymer has a marginal effect on the solubility of hydrogen.

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