# Solubility of Hydrogen in Aqueous Solution of 2-Butyne-1,4-diol and 2-Butene-1,4-diol†

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**The solubility of hydrogen in aqueous solutions of 2-butyne-1,4-diol and 2-butene-1,4-diol is determined at temperatures between 30 and 90 °C, pressures between 7.7 and 48.5 atm, and concentrations between 1 and 10 M. Gas solubilities followed Henry's law over the entire range of data, and proper coefficients are reported.**

The purpose of this study is to determine the solubility of hydrogen in aqueous solutions of 2-butyne-1,4-diol and 2-butene-1,4-diol under various conditions of temperature, pressure, and solute concentrations. The data are important in modeling a slurry reactor for the hydrogenation of 2-butyne-1,4-diol to 2-butene-1,4-diol as well as determining the solute influence on solubility.

No data have been reported in the literature for the solubility of hydrogen in aqueous solutions of 2-butyne-1,4-diol and 2-butene-1,4-diol. Solubility of hydrogen in 2-butyne-1,4-diol and 2-butene-1,4-diol was studied in the range of interest for hydrogenation, namely, 30–90 °C, 7.7–48.5 atm, and 1–10 M concentration.

The solutions were prepared from degassed and deionized water. 2-Butyne-1,4-diol and 2-butene-1,4-diol (Fluka) of 99% purity were used directly for preparing solutions of desired concentrations. Hydrogen gas supplied by IOL with a purity of more than 99.9% was used in all of the measurements. The experimental setup and procedure was similar to that of Wisniak et al. (*1*). The setup was simple and provided precise measurements in comparison with other techniques. The equilibrium cell used in this work consisted of a Parr 2-L stirred autoclave provided with automatic heating control instruments and an internal cooling coil. The solution was allowed to equilibrate for at least 2 h to ensure complete mixing. The maximum experimental error was found to be less than 3% for most of the data points.

The accuracy and the reliability of the equipment and the procedure were determined by measurement of solubility of hydrogen in pure water at 50 and 100 °C and at 25-atm partial

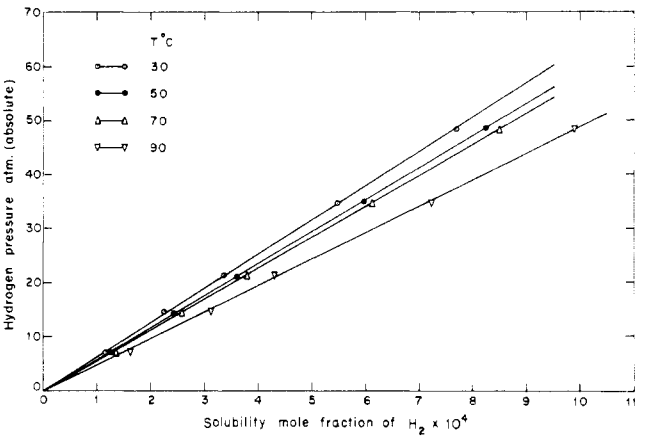


**Figure 1.** Solubility of hydrogen in 5.65 M 2-butyne-1,4-diol.

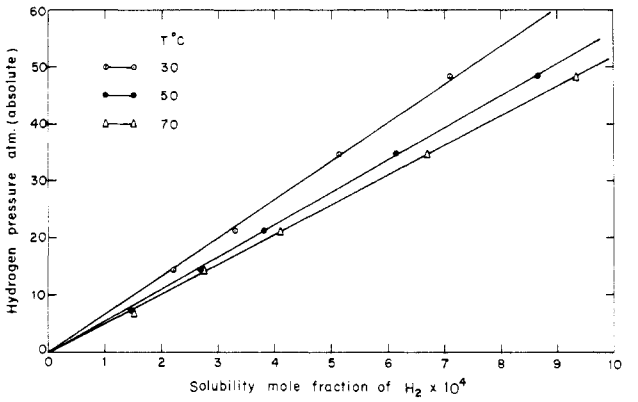


**Figure 2.** Solubility of hydrogen in 4.63 M 2-butene-1,4-diol.

Table I. Solubilities and Henry's Constants

| compd | molarity | temp, °C | $10^{-4}$H, atm (mole fraction)$^{-1}$ | solubility, mole fraction of $H_2$ X $10^4$ | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 7.7 atm | 14.5 atm | 21.3 atm | 34.9 atm | 48.5 atm |
| 2-butyne-1,4-diol | 1.082 | 30 | 7.880 | 0.928 | 1.80 | 2.75 | 4.42 | 6.12 |
| | | 50 | 7.814 | 0.964 | 1.91 | 2.80 | 4.48 | 6.20 |
| | | 70 | 7.570 | 1.00 | 1.98 | 2.85 | 4.63 | 6.40 |
| | 3.220 | 30 | 7.730 | 1.00 | 1.85 | 2.80 | 4.45 | 6.30 |
| | | 50 | 6.336 | 1.20 | 2.25 | 3.36 | 5.54 | 7.62 |
| | | 70 | 6.110 | 1.28 | 2.38 | 3.53 | 5.70 | 7.95 |
| | 5.652 | 30 | 6.289 | 1.15 | 2.25 | 3.35 | 5.47 | 7.70 |
| | | 50 | 5.850 | 1.25 | 2.42 | 3.60 | 5.95 | 8.25 |
| | | 70 | 5.705 | 1.35 | 2.55 | 3.80 | 6.12 | 8.50 |
| | | 90 | 4.900 | 1.63 | 3.10 | 4.30 | 7.22 | 9.90 |
| | 10.210 | 30 | 4.680 | 1.56 | 3.16 | 4.75 | 7.30 | 10.40 |
| | | 50 | 4.158 | 2.00 | 3.51 | 5.36 | 8.40 | 11.73 |
| | | 70 | 3.739 | 2.20 | 4.19 | 5.97 | 9.40 | 13.07 |
| 2-butene-1,4-diol | 4.633 | 30 | 6.880 | 1.26 | 2.20 | 3.30 | 5.13 | 7.10 |
| | | 50 | 5.660 | 1.45 | 2.69 | 3.82 | 6.15 | 8.64 |
| | | 70 | 5.200 | 1.55 | 2.75 | 4.09 | 6.70 | 9.35 |
| | 11.796 | 30 | 1.757 | 4.73 | 8.44 | 12.19 | 20.28 | 27.60 |
| | | 50 | 1.580 | 4.94 | 9.40 | 14.13 | 22.41 | 30.60 |
| | | 70 | 1.440 | 5.40 | 10.10 | 15.40 | 24.54 | 33.41 |

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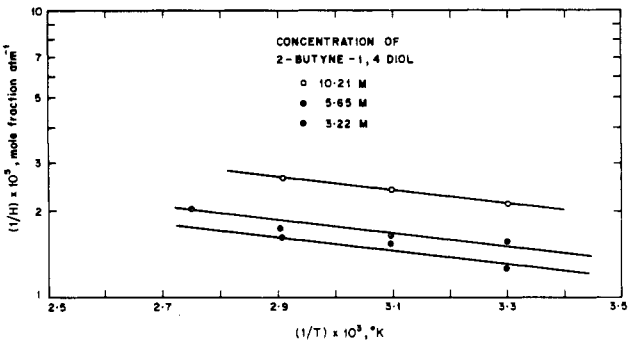


**Figure 3.** Temperature dependence of Henry's law constant in 2-butyne-1,4-diol solutions.

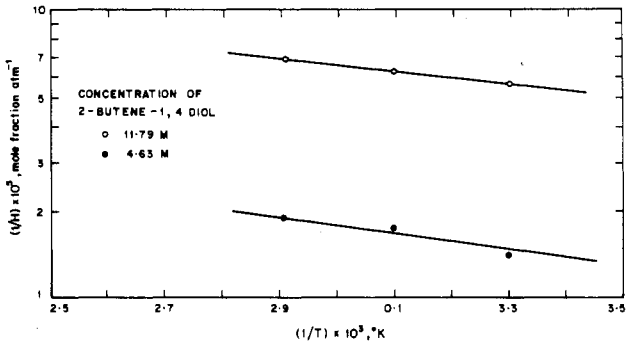


**Figure 4.** Temperature dependence of Henry's law constant in 2-butene-1,4-diol solutions.

pressure of hydrogen. The values of the Henry's law constant (in atm (mole fraction)$^{-1}$) obtained as $7.7 \times 10^4$ at 50 °C and $6.7 \times 10^4$ at 100 °C agreed quite well with those reported by Wiebe et al. (*2*) and Wilhelm et al. (*3*).

The experimental data are presented in Table I, and Figures 1 and 2 show some typical curves of solubility as a function of total pressure. Henry's law, $H = p/x$, where H represents the Henry's law constant (atm (mol fraction)$^{-1}$), $p$ is the partial pressure of hydrogen (atm), and $x$ is the solubility of hydrogen (mol fraction), is satisfied in every case up to the highest pressure tested, and Table I summarizes the values of Henry's law constants. The constants were determined from least-squares fit of the data.

An examination of Table I shows that, for given concentrations of 2-butyne-1,4-diol and 2-butene-1,4-diol, hydrogen solubility increases with an increase in temperature. The influence of temperature on the solubility of hydrogen in 2-butyne-1,4-diol and 2-butene-1,4-diol solutions is shown in Figures 3 and 4 as plots of ln 1/H vs. $1/T$. The solubility was found to be a mild function of temperature. The average values of $\Delta H$, partial molar enthalpy, obtained from Figures 3 and 4 for hydrogen–2-butyne-1,4-diol–water and hydrogen–2-butene-1,4-diol–water systems were 1135 and 1098 cal g-mol$^{-1}$, respectively. The solubility of hydrogen is enhanced by solutes considered here.

## Literature Cited

† NCL Communication No. 2744.
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(3) Wilhelm, R.; Battino, R.; Wilcock, R. J. *Chem. Rev.* **1977**, *77*, 219.

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