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Hydrogen Solubility in Aqueous Solutions of Sugars and Sugar Alcohols

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The solubility of hydrogen in aqueous solutions of sugars and their alcohols is determined at temperatures between 80° and 120°C, pressures between 100 and 800 psig, and molar concentrations between 0.5 and 3. Henry's Law is observed in every case, and the proper coefficients are reported.

The purpose of this study is to determine the solubility of hydrogen in aqueous solutions of sugars and sugar alcohols, under various conditions of pressure, temperature, and solute concentration. The data are important for obtaining a better estimate of the hydrogen concentration at the catalyst surface when hydrogenating the sugars, as well as determining the solute influence on solubility.

The solubility of hydrogen in water and organic and inorganic solutions has been studied extensively (1), although not with the compounds employed in this work. Lyashch (2) reported that the solubility of CO_2 in sucrose solutions decreased strongly with an increase in solute concentration, whereas an opposite effect was observed with citric acid. Wiebe et al. (4) found that the isothermal solubility of hydrogen in water showed a minimum between 40° and 60°C for pressures up to 1000 atm.

Experimental

Solubility effects were studied in the range of interest for hydrogenation, namely, 80–120°C, 100–800 psig, and 0.5–3.0M concentration. The solutions were prepared from distilled water and commercially available solutes (Sigma), 99.9% pure as reported by the manufacturer.

The equilibrium cell used in this work consisted of a ¾ gal. high-pressure autoclave manufactured by Autoclave Engineers, provided with automatic heating control instrument and an internal cooling coil. By proper use of both elements, it was possible to control the solution temperature to ±1°C. The autoclave was connected to a solubility measuring train similar to that used by Wiebe et al. (4) for the determination of the solubility of hydrogen in water at high pressures.

The apparatus (Figure 1) consisted essentially of two gas burets (1, 2) immersed in a water bath (4) that could be controlled to ±0.1°C. Both burets had a capacity of 100 ml with 0.2-ml graduations. The buret on the right (2), or solution buret, was connected through its bottom end to a tee. One opening of the tee connected to a lev-

eling bulb (6) filled with solution of the appropiate concentration, and the other opening of the tee was connected to a high-pressure valve (B). The leveling bulb line was provided with a stopcock (D) so that the liquid level inside the solution buret could be adjusted to any level. A ⅜-in. diameter, high-pressure stainless-steel tubing (10) connected the high-pressure valve (B) to the sample line of the autoclave. This high-pressure line also had a branch with another high-pressure valve (A) so that the autoclave connecting line could be purged when desired.

The buret on the left (1), or hydrogen buret, was also provided with a stopcock (C) and a leveling bulb filled with mercury (5). The burets were connected at the top to a glass tee that led to a two-way stopcock (E). One opening of the stopcock (E) connected the buret system to the atmosphere while the other opening connected the system to a mercury manometer (3).

The autoclave was loaded with a solution of the proper molarity, pressurized to the desired level (±10 psig), and heated under agitation until the proper temperature, ±1°C, was attained for at least 15 min. The solubility ap-
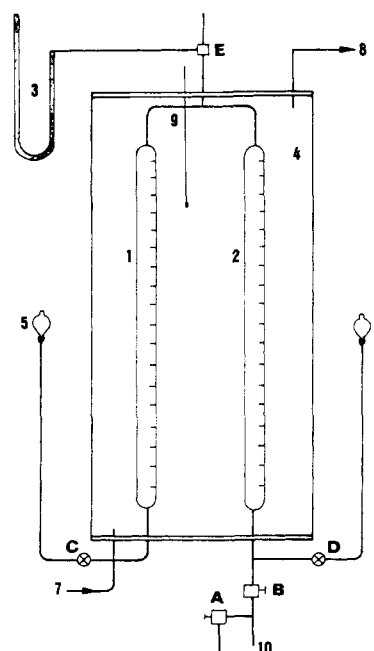

Figure 1. Solubility apparatus

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paratus was next prepared for a measurement. To do so, the solution level in the solution buret (2) was adjusted to zero mark by means of the leveling bulb (6). The upper stopcock (E) was positioned to connect the buret system to the atmosphere. The mercury leveling bulk (5) was then raised to such a position that the mercury would flow into the gas buret (1) to a reading of 70–90 ml, depending on the size of the solution-hydrogen sample to be taken. Stopcock (E) was then turned to connect the buret system to the mercury manometer (3). The mercury leveling bulb was readjusted, when necessary, so that the manometer would be at equilibrium with atmospheric pressure. Atmospheric pressure and the water jacket temperature were then recorded. With these manipulations, the solubility apparatus was ready to receive the sample.

Since the high-pressure line was at a different temperature than that of the autoclave, the line was flushed through purge valve (A) with about 20 ml of the apparatus. This valve was then closed, and the agitator stopped. Valve (B) was cracked open to allow a small sample of solution to flow from the autoclave to the oil buret (2). The sample size varied between 20 and 50 ml, depending on the pressure in the autoclave. As soon as the required volume of solution was admitted, valve (B) was closed. Hydrogen began flashing immediately from the solution, and the pressure increased inside the buret system. To eliminate leaks, the mercury leveling bulb (5) was lowered at a proper rate to insure that atmospheric pressure was maintained in the buret system, as indicated by the mercury manometer (3).

When no more hydrogen bubbles were seen in the liquid phase, the mercury leveling bulb was adjusted to a final position which indicated exactly the atmospheric pressure in the apparatus. Between 15–30 min were necessary to flash the hydrogen completely. The levels of liquid in both burets were recorded together with the values of atmospheric pressure, water jacket temperature, and autoclave temperature and pressure. With these figures the solubility of hydrogen was readily calculated.

Results and Discussion

As a check of the experimental techniques, the solubility of hydrogen in pure water at 300°F was determined at three pressures. The value of Henry's constant obtained, 25, agreed well with that reported by Pray et al. (3).

The readings of the solubility train were converted to Kuenen's coefficients, S, ml of gas at STP/g H_2O, by use
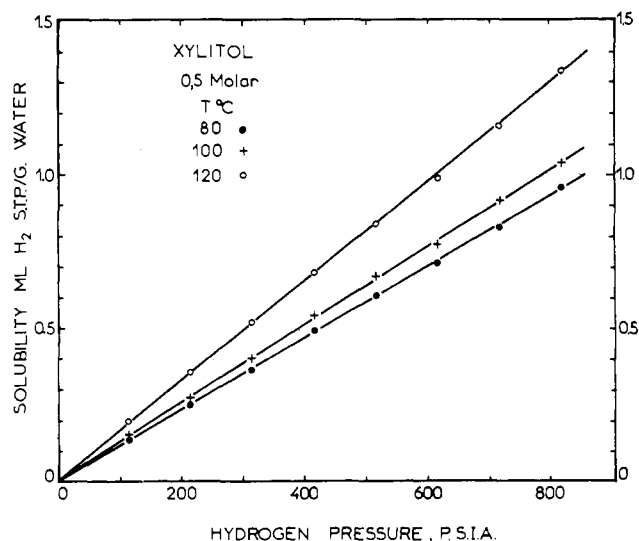

Figure 2. Solubility of hydrogen in xylitol 0.5M

Table I. Solubilities and Henry's Constants

| Compound | M | Temp, °C | H | S Press, psig | | | | | | | |
				100	200	300	400	500	600	700	800
Xylose	0.5	80	22.8	0.149	0.269	0.390	0.505	0.637	0.759	0.878	1.015
		100	24.2	0.147	0.275	0.418	0.539	0.681	0.818	0.937	1.078
		120	28.8	0.190	0.343	0.507	0.649	0.800	0.967	1.117	1.281
	2.0	80	28.4	0.170	0.340	0.480	0.619	0.790	0.941	1.077	1.230
		100	23.6	0.149	0.284	0.404	0.537	0.694	0.792	0.923	1.055
		120	27.3	0.165	0.319	0.471	0.621	0.772	0.917	1.057	1.216
	3.0	100	28.8	0.175	0.358	0.496	0.677	0.829	0.979	1.060	1.297
		120	29.5	0.188	0.331	0.500	0.670	0.836	0.957	1.122	1.287
Xylitol	0.5	80	21.4	0.140	0.253	0.363	0.495	0.611	0.714	0.831	0.965
		100	23.3	0.153	0.274	0.401	0.542	0.669	0.774	0.918	1.038
		120	29.9	0.200	0.360	0.520	0.681	0.843	0.990	1.162	1.337
	2.0	80	27.9	0.168	0.325	0.483	0.626	0.774	0.928	1.110	1.229
		100	30.0	0.187	0.364	0.512	0.677	0.851	1.001	1.174	1.334
		120	31.9	0.199	0.368	0.549	0.740	0.913	1.087	1.236	1.419
	3.0	80	25.9	0.175	0.316	0.446	0.584	0.726	0.880	1.017	1.155
		100	25.8	0.167	0.301	0.436	0.568	0.737	0.861	1.034	1.176
		120	27.9	0.174	0.340	0.478	0.623	0.789	0.924	1.085	1.252
Sorbitol	0.5	80	21.6	0.135	0.259	0.370	0.490	0.624	0.730	0.848	0.965
		100	27.5	0.160	0.296	0.445	0.587	0.729	0.853	0.999	1.157
		120	26.4	0.155	0.316	0.453	0.582	0.728	0.898	1.031	1.174
	2.0	80	23.9	0.152	0.285	0.404	0.565	0.677	0.805	0.947	1.062
		100	23.7	0.153	0.276	0.400	0.544	0.657	0.787	0.930	1.059
		120	28.4	0.180	0.314	0.477	0.660	0.804	0.982	1.118	1.275
Mannitol	0.5	80	22.1	0.140	0.264	0.377	0.497	0.622	0.742	0.965	0.980
		100	24.7	0.160	0.292	0.429	0.558	0.704	0.840	0.976	1.101
		120	26.9	0.169	0.317	0.463	0.612	0.770	0.913	1.055	1.207

of the density and vapor pressure of the solution at the appropiate water jacket temperature. S is low enough that it can be converted to mole fraction, multiplying by the factor 18/22,414. Plots of S against the absolute pressure indicated that Henry's Law was satisfied in every case up to the highest pressure tested. Table I summarizes the values of S and Henry's constant H, atm/mole fraction (best slope), and Figure 2 shows some typical curves. Each value in Table I is the average of at least three measurements.

The major sources of error in this work were associated with the measurement of pressure and temperature inside the equilibrium cell and the gas and liquid volumes in the burets. The latter could be read to within 0.1 ml so that it is estimated that the data presented here are accurate to within 3–5%, the lowest inaccuracy corresponding to the lower pressures.

An examination of Table I shows that for a given concentration, hydrogen solubility increases with increasing temperature for practically every case, within the experimental error. The only significant anomaly is for xylose solutions 2M. Salting effects at constant temperature and pressure depend on the solute and its concentration; thus, for increased molarity the solubility of xylitol goes through a maximum, whereas that of xylose goes through a minimum.

The variation of Henry's constant with temperature does not follow a regular pattern with changes in molarity. Although this is not the expected behavior, several literature references (1) indicate that for light gases, the sign of the temperature derivative of Henry's constant varies with solute concentration. Apparently, for polyhydric alcohols the changes with temperature of surface tension, density, and solvation follow a more complicated pattern.

The solubility of hydrogen in pure water at 100°C and 50 atm is 0.9116 ml STP/g water (4); thus, it is enhanced by the solutes here considered.

Solutions of concentration 3M were extremely viscous and did not allow repetitive determination.

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Vapor-Liquid Equilibria at 1 Atm.   Systems Containing n-Hexane, Methylcyclopentane, Ethyl Alcohol, and Benzene

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Vapor-liquid equilibrium data at 1 atm are presented for the ternary system n-hexane–methylcyclopentane–benzene and the quaternary system involving ethyl alcohol. The data are believed accurate to ±0.04°C and ±0.2 mol % with respect to temperature and composition, respectively. Multicomponent predictions based upon binary constants agree with the experimental data.

To study tray efficiencies in distillation columns not only requires accurate vapor-liquid equilibrium data but also a mathematical model for predicting additional values as well. Hence, prior to the determination of the reported tray efficiencies (12, 13) in binary, ternary, and quaternary systems containing n-hexane, methylcyclopentane (MCP), ethyl alcohol, and benzene, the ternary and quaternary data of Weber et al. (1, 2, 8, 10) were subjected to further analysis utilizing the Wilson equation (11) as modified by Oyre and Prausnitz (4). These previous investigations reported temperature and composition measurements accurate within ±0.1°C and ±0.5 mol %, respectively.

The purposes here are to present the new, more accurate data which were obtained for the tray efficiency investigation and to show the comparative results with the same analytical treatment mentioned above. These new data are believed accurate to ±0.04°C and ±0.2 mol % regarding temperature and composition, respectively.

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Experimental

The benzene and MCP were pure grade (minimum 99 mol % purity) materials, and the n-hexane was technical grade (97.3 mol %). The major impurity (2.43%) in the straight-chain paraffin was MCP (9), which meant the purity was 99.7% with respect to the n-hexane–MCP system. These hydrocarbons were obtained from the Phillips Petroleum Co. The absolute alcohol was manufactured by USI, and glc analysis indicated only a trace amount of impurities. The chemicals were passed through a Perkin-Elmer 880 chromatograph equipped with a hot wire detector, a 194B printing integrator, and a Leeds and Northrup Speedomax G strip chart recorder. In no case did extraneous peaks appear. Within the accuracy of the glc analysis, the MCP was confirmed to be 99.8% pure with 0.2% n-hexane (12).

A modified Braun equilibrium still was used to obtain the experimental data. Equipment and procedures were similar to those of Lee (3). An iron–constantan thermocouple in conjunction with a Leeds and Northrup-type K potentiometer permitted temperature measurements with a probable error (7) of ±0.04°C.

The equilibrium pressure was measured by a manometer and was maintained at 760 ± 0.1 mm of mercury. The pressure above existing atmospheric pressure was obtained by bleeding nitrogen into the equilibrium still. The flow of nitrogen was controlled by a manostat.

Ternary and quaternary samples were analyzed by glc. Helium was the carrier gas. The ternary system was analyzed with a 10-ft column ($\frac{1}{8}$-in. o.d.) with solid support