

Hydrogen Solubility in Jojoba Oil

JAIME WISNIAK and SHOSHANAH STEIN, Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel

ABSTRACT

The solubility of hydrogen in jojoba oil has been determined at temperatures of 50-250 C and pressures between 100-800 psig. The system behaves according to Henry's law with a heat of solution of 1240 cal/g mole and entropy of solution of 2.9 cal/K g mole. The partial volume of hydrogen varies between 24.6-62.9 ml/g mole in the temperature range considered.

INTRODUCTION

The purpose of this study was to determine the solubility of hydrogen in jojoba oil (*Simmondsia californica*) under a wide range of temperature and pressure conditions. The data were of importance for obtaining a better estimate of the hydrogen concentration at the nickel catalyst surface when hydrogenating the oil.

Jojoba is unique among plants in that its seed contains ca. 50% by wt of a practically colorless, odorless oil composed of the straight chain esters of the C₂₀ and C₂₂ alcohols and acids with one double bond. *Simmondsia* oil resembles sperm oil in chemical composition and behavior, and, if a sufficient supply were available at a competitive price, it undoubtedly could find use as a substitute for sperm oil and high priced waxes like carnauba and beeswax. The liquid can be hydrogenated easily to a highly lustrous, pearly white crystalline laminae, with a mp of ca. 70-75 C, resembling carnauba wax. Partial hydrogenation yields a softer wax which, like the liquid and completely hydrogenated product, has unusual stability during long storage. Various uses have been suggested for the wax, e.g. as an ingredient in polish waxes, carbon paper, penicillin drugs, waxing of fruit, and the impregnation of heat-resistant paper containers (1).

The solubility of gases in liquids has been under quantitative study for many years, but very few data have been published in the literature on the solubility of hydrogen in fatty materials. Tyntyunnikov and Novitskaya (2) found that, at atmospheric pressure, the solubility of hydrogen in oils like apricot, castor oil, sunflower, and hydrogenated sunflower varied from 4-5.3 ml standard temperature and pressure (STP)/100 g at 50 C and from 6.3-8.6 ml STP/100 g at 220 C. Tomoto and Kusano (3) measured the solubility of hydrogen, nitrogen, and oxygen in soybean oil at pressures between 0.2-1 atm and temperatures between 30-70 C. Under these conditions, they found that the system behaved according to Henry's law and that the solubility decreased with increased temperatures. The differential heat of solution was calculated to be -3.86 Kcal/mole. Wisniak and Albright (4) measured the solubility of hydrogen in cottonseed oil at pressures between 100-1500 psig and temperatures between 50-140 C and found that the solubility increased with increased temperatures and that Henry's law was satisfied up to 500 psia.

MATERIALS AND METHODS

Solubility effects were studied in the range of interest for hydrogenation, namely 50-250 C and 100-800 psig. The jojoba seeds obtained in this work were obtained from shrubs grown at the Negev Institute for Arid Zone Research, now a part of the Ben-Gurion University of the Negev. Cold pressing produced a medium color oil that had

the following characteristics: refractive index (20 C), 1.4652; iodine value (Wijs), 83.2; mp, 13.0 C; acid number, 6.7; saponification number, 107. The gas chromatographic analysis performed according to the method suggested by Miwa (5) gave the following results: C₃₄, 0.1%; C₃₆, 1.6%; C₃₈, 7%; C₄₀, 32%; C₄₂, 49%; C₄₄, 9%; C₄₆, 0.9%; and C₄₈, 0.1%. The oil was used as such without further purification. Hydrogen was 99.9% pure as reported by the vendor.

The equilibrium cell used in this work consisted of a three-fourth gallon, high pressure autoclave manufactured by Autoclave Engineers, Erie, Pa., 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 ± 0.5 C. The autoclave was connected to a solubility measuring train similar to that em-

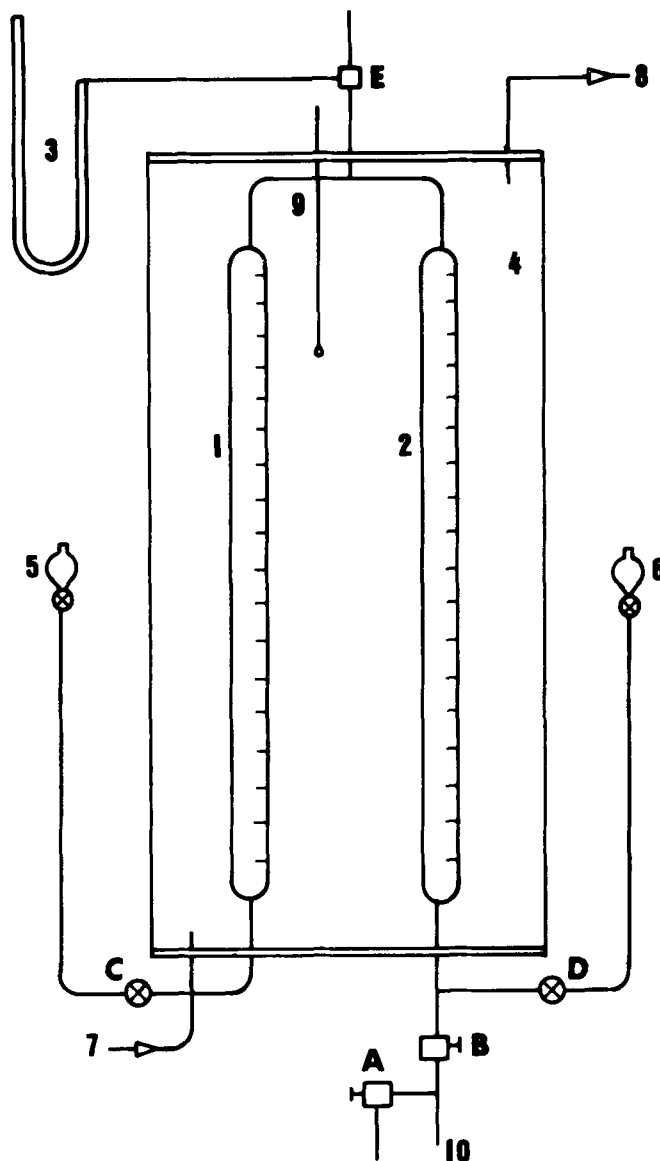


FIG. 1. Solubility apparatus: Gas burette 1, oil burette 2, mercury manometer 3, water bath 4, mercury leveling bulb 5, oil leveling bulb 6, constant temperature water inlet and outlet 7,8, thermometer 9, purge 10, and valves A,B,C,D,E.

ployed by Wiebe, et al., (6) for the determination of the solubility of hydrogen in water at high pressures.

The apparatus (Fig. 1) consisted essentially of two gas burettes (1,2 in figure) immersed in a water bath (4 in figure) that could be controlled to ± 0.1 C. Both burettes had a capacity of 100 ml with 0.2 ml graduations. The burette on the right (2 in figure), or oil burette, was connected through its bottom end to a tee. One opening of the tee connected to a leveling bulb (6 in figure) filled with oil and the other opening of the tee was connected to a high pressure valve (B in figure). The leveling bulb line was provided with a stopcock (D in figure) so that the liquid level inside the solution burette could be adjusted to any level. A three-eighth in. diameter high pressure stainless steel tubing (10 in figure) connected the high pressure valve (B in figure) to the sample line of the autoclave. This high pressure line also had a branch with another high pressure valve (A in figure) so that the autoclave connecting line could be purged when desired.

The autoclave was loaded with ca. 1 liter oil, pressurized to the desired level (± 10 psig) and heated under agitation until the proper temperature was attained for at least 30 min. The solubility apparatus was next prepared for a measurement. To do so, the solution level in the solution burette (2 in figure) was adjusted to zero mark by means of the leveling bulb (6 in figure). The upper stopcock (E in figure) was positioned to connect with burette system to the atmosphere. Mercury leveling bulb (5 in figure) then was raised to such a position that the mercury would flow into the gas burette (1 in figure) to a reading of 70-90 ml, depending upon the size of the solution-hydrogen sample to be taken. Stopcock (E in figure) then was turned to connect the burette system to the mercury manometer (3 in figure). 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 then were 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 in figure) with ca. 20 ml through valve (A in figure) before introducing the solution sample in the apparatus. This valve then was closed and the agitator stopped. Valve (B in figure) was cracked open to allow a small sample of solution to flow from the autoclave to the oil burette (2 in figure). The sample size varied between 20-50 ml, depending upon the pressure in the autoclave. As soon as the required value of solution was admitted, valve (B in figure) was closed. Hydrogen began flashing immediately from the solution, and the pressure increased inside the burette system. To eliminate leaks, the mercury leveling bulb (5 in figure) was lowered at a proper rate to ensure that atmospheric pressure was maintained in the burette system, as indicated by the mercury manometer (3 in figure).

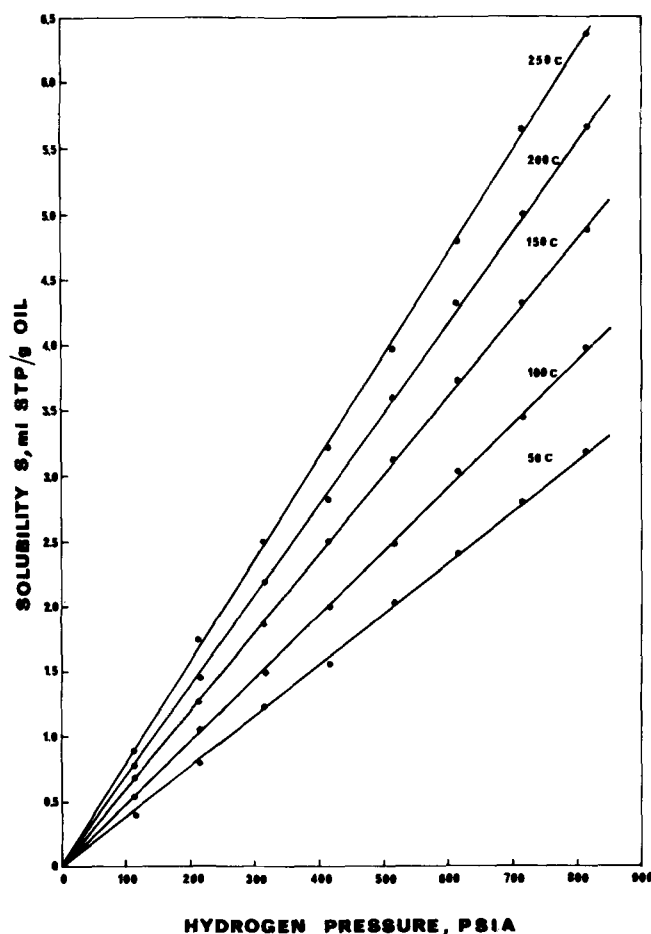


FIG. 2. Solubility of hydrogen. STP = standard temperature and pressure.

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 flush the hydrogen completely. The levels of liquid in both burettes 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 calculated readily.

RESULTS AND DISCUSSION

The readings of the solubility train were converted to Kuenen's coefficient S , ml gas at STP/g oil, using the density of the oil at the jacket temperature and the barometric reading. The values of S can be converted easily to mole fraction using the value of 606 for the mol wt of the oil. Plots of S against the absolute pressure were linear for every

TABLE I
Hydrogen Solubility in Jojoba Oil^a

Pressure psig	Temperature									
	50		100		150		200		250	
	S	x_2	S	x_2	S	x_2	S	x_2	S	x_2
110	0.44	0.0118	0.56	0.0150	0.68	0.181	0.80	0.0212	0.91	0.0240
200	0.84	0.0222	1.06	0.0280	1.28	0.0333	1.49	0.0387	1.69	0.0437
300	1.21	0.0324	1.50	0.0400	1.88	0.0484	2.20	0.0562	2.46	0.0624
400	1.61	0.0417	2.00	0.0513	2.50	0.0634	2.83	0.0711	3.23	0.0803
500	2.00	0.0513	2.51	0.0635	3.11	0.0776	3.58	0.0882	4.01	0.0979
600	2.41	0.0611	3.00	0.0750	3.70	0.0910	4.29	0.104	4.80	0.115
700	2.78	0.0700	3.49	0.0863	4.32	0.105	4.98	0.119	5.58	0.131
800	3.18	0.0792	3.97	0.0970	4.90	0.116	5.64	0.132	6.37	0.147

^aSmoothed values.

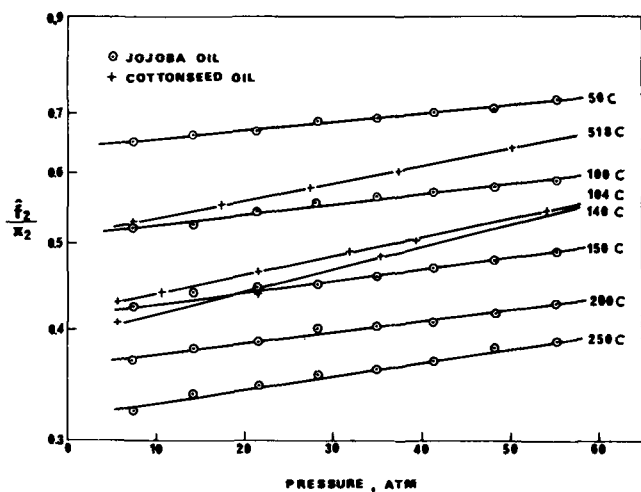


FIG. 3. Test of the equation of Krichevsky and Kasarnovsky.

temperature up to the highest pressure tested. Table I summarizes the values of S and x_2 and Figure 2 plots the isothermal variation of S with pressure. Each value in Table I is the average of at least three measurements. It is seen that the solubility increases with increased temperature and that the molar fraction of hydrogen grows to ca. 0.15.

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 oil volumes in the burettes. It is estimated that the data presented here are accurate to within 1-2%, the lowest inaccuracy corresponding to the lower pressure.

The data obtained can be subjected to the following thermodynamic analysis (7).

The condition for equilibrium at constant temperature and pressure is:

$$\hat{f}_2 \text{ gas} = \hat{f}_2 \text{ liq.} \quad \text{[I]}$$

The fugacity of the gas is related to the solubility through Henry's law:

$$\hat{f}_2 = \gamma_2^* H x_2, \quad \text{[II]}$$

where by definition

$$H = \lim_{x_2 \rightarrow 0} \hat{f}_2 / x_2 \quad (\text{constant } T) \quad \text{[III]}$$

and γ_2^* is the activity of the dissolved hydrogen normalized so that:

$$\lim_{x_2 \rightarrow 0} \gamma_2^* = 1. \quad \text{[IV]}$$

Equation II together with the rigorous relation:

$$(\partial \ln \hat{f}_2 / \partial P)_{T, x} = \bar{v}_2 / RT \quad \text{[V]}$$

leads to the Krichevsky and Kasarnovsky equation (8):

$$\ln \hat{f}_2 / x_2 = \ln H + \bar{v}_2^{\infty} (P - P_1^0) / RT$$

Equation VI was obtained under the assumption that the partial molar volumes \bar{v}_2^{∞} and γ_2^* are independent of the pressure and the solute concentration. The latter condition may

be removed by assuming any of the usual expressions for γ_2 as a function of concentration.

In the particular case under consideration, the solvent is nonvolatile so that $P_1^0 = 0$ and \hat{f}_2 may be identified with the fugacity of pure hydrogen (9).

The validity of equation VI was tested on a semilog plot, as shown in Figure 3. The values of \bar{v}_2^{∞} and H , as obtained from the slope and the intercept, are reported in Table II for the five temperature levels examined.

The data of Wisniak and Albright (4) for cottonseed oil were reexamined under the same criteria and also are reported in Figure 3 and Table II. It can be seen that the partial molar volume of hydrogen has similar values in both oils and that the gas is more soluble in jojoba oil than in cottonseed oil.

The heat of solution and the entropy of solution of hydrogen can be evaluated through the strict relations:

$$(\partial \ln H / \partial 1/T)_P = -\Delta \bar{H}_2 / R \quad \text{[VII]}$$

$$(\partial \ln x_2 / \partial \ln T)_P = \Delta \bar{S}_2 / R. \quad \text{[VIII]}$$

Plots of $\ln H$ against the reciprocal of the temperature gave straight lines indicating that the heats of solution were independent of temperature over the range studied here. Values of $\Delta \bar{H}_2$ calculated from the smoothed data were 1240 cal/g mole for jojoba oil and 836 cal/g mole for cottonseed oil, similarly log-log plots of x_2 against T for jojoba oil gave a set of parallel lines for the 8 pressure levels tested. From them, it was calculated that the partial entropy of solution is 2.9 cal/K. g mole.

APPENDIX

\hat{f}_2	= Fugacity of hydrogen in solution, atm.
H	= Henry's constant, atm.
$\Delta \bar{H}_2$	= Molar heat of solution of hydrogen, cal/g mole.
P	= Pressure, atm.
P_1^0	= Vapor pressure of solvent.
R	= Gas constant, cal/K g mole.
S	= Kuenen coefficient, ml standard temperature and pressure/g.
$\Delta \bar{S}_2$	= Partial molar entropy change of hydrogen, cal/K g mole.
T	= Absolute temperature, K.
\bar{v}_2	= Partial molar volume of hydrogen, ml/g mole.
\bar{v}_2^{∞}	= Partial molar volume of hydrogen at infinite dilution, ml/g mole.
x_2	= Mole fraction of hydrogen in the oil phase.
γ_2^*	= Activity coefficient of hydrogen, normalized.

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REFERENCES

- Daugherty, P.M., H.H. Sineath, and T.A. Wastler, *Econ. Bot.* 12:296 (1958).
- Tyutynikov, B.N., and I.I. Novitskaya, *Maslobo Zhir. Prom.* 23:13 (1957).
- Tomoto, N., and K. Kusano, *Yukagaku* 16:108 (1967).
- Wisniak, J., and L.F. Albright, *Ind. Eng. Chem.* 53:375 (1961).
- Miwa, T., *JAOCS* 48:259 (1971).

TABLE II

Thermodynamic Parameters

Jojoba oil			Cottonseed oil		
Temperature, C	Henry's constant, atm	\bar{v}_2^{∞} (ml/g mole)	Temperature, C	Henry's constant, atm	\bar{v}_2^{∞} (ml/g mole)
50	640	24.6	51.8	510	26.2
100	510	34.4	104	420	32.8
150	420	42.9	140	393	43.3
200	365	49.5	--	--	--
250	320	62.9	--	--	--

6. Wiebe, R., V.L. Gaddy, and C. Heins, *Ind. Eng. Chem.* 24:823 (1932).
7. Prausnitz, J.M., "Molecular Thermodynamics of Fluid-Phase Equilibria," Prentice-Hall, Englewood Cliffs, N.J., 1969, p. 356.
8. Krichevsky, I.R., and J.S. Kasarnovsky, *J. Am. Chem. Soc.*

- 57:2168 (1935).
9. Deming, W.E. and L.E. Shupe, *Phys. Rev.* 40:848 (1932).

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