Solubility of Some Light Hydrocarbons and Hydrogen in Some Organic Solvents

J. A. WATERS, GEORGE A. MORTIMER, and H. E. CLEMENTS[1]
Monsanto Co., Texas City, Tex. 77591

The solubilities of hydrogen and some light hydrocarbons in *n*-hexane, toluene, and 1,2-dichloroethane at pressures of 1 atm. or less and temperatures of −23° to 25° C. were determined. The data were compared with published values, and discrepancies for hydrogen in 1,2-dichloroethane and for ethylene in toluene in the existing literature resolved. Relevant vapor pressures of the solvents were also measured.

THE SOLUBILITIES of hydrogen, ethylene, ethane, and propane in binary systems with toluene, as well as the solubilities of hydrogen and ethylene in *n*-hexane and 1,2-dichloroethane, are reported here. Some of the data are new, whereas others resolve discrepancies in existing literature data. Some new vapor pressure data for 1,2-dichloroethane were also obtained.

EXPERIMENTAL

Apparatus and Procedure for Measuring Solubilities. Two types of apparatus were used for solubility measurements. In both pieces of apparatus the gas absorbed by a given volume of solvent was measured by measuring the pressure change in a reservoir of known volume. The uptake of gas was checked in some cases by weighing the solvent before and after introduction of the gas.

Apparatus and Method A. The apparatus consisted of two glass bulbs connected by 1/4-inch stainless steel tubing fitted with Hoke valves, gas and vacuum inlets, and a strain gage (Statham Instruments, Los Angeles, Calif.). The signal from the strain gage was measured by a K-3 Universal potentiometer (Leeds & Northrup, Philadelphia, Pa.) and gave pressure readings accurate to ±0.1 mm. of mercury. A constant temperature oil bath, controlled by a circulating glycol stream from a constant temperature unit (Forma Scientific, Marietta, Ohio), was used to control the temperature of the solvent-gas mixture. The temperature of the bath was measured by a platinum resistance thermometer in conjunction with a Mueller bridge and a 1-mv. recorder (both from Leeds & Northrup). Temperature measurements were accurate to ±0.01° C.

The solvent (100 ml.) was first degassed three times at liquid nitrogen temperature in a bulb, *a* (337.4 ml.), which contained a magnetic stirring bar. The vapor pressure of the solvent was then measured by opening the bulb to the pressure-measuring system and stirring the solvent while the bulb was held at constant temperature in the oil bath. The second bulb, *b*, and connecting tubing were filled to a known pressure at room temperature and a valve was then opened to allow the gas to expand into bulb *a* containing the solvent and its vapor only. In initial runs, erratic results were obtained with hydrogen because of adsorption of the gas on the walls of bulb *a*. A correction for this was made by admitting gas to the bulb without stirring the solvent, recording the pressure as a function of time, and extrapolating to zero time. The gas uptake was calculated using Charles' law.

Method B. The apparatus is shown schematically in Figure 1. The chief components were a steel bomb, *c*, a Heise gage (0 to 14 atm.), *d*, two regulators, *e* and *f* (Fisher-Governor Co., Marshalltown, Iowa), a manometer, *g*, and a 500-ml. flask, *h*, fitted with a magnetic stirring bar, *y*, immersed in a bath, *j*. The flask was fitted with a stopcock, *k*, and ball connecting joint, *l*. The second regulator, *f*, was adjusted to regulate from above atmospheric pressure down to 100 mm. of mercury.

For measurements at 0° C. the temperature of the solvent was controlled by immersion in ice, and at −20° C. by a Cellosolve bath in which dry ice chips were periodically placed. For measurements at room temperature a water bath with no temperature control was used. The temperatures were recorded with a thermometer graduated in 0.1° divisions.

The volumes of bomb *c* and flask *h* were measured by measuring the increase in weight when filled with water at a known temperature. The volumes of the gage and 1/4-inch stainless steel piping were then determined by the usual pressure-change measurements.

In a solubility determination, the solvent (400 ml.) was degassed at −78° C. and then stirred at the desired temperature with stopcock *k* closed. The bomb and gage were filled with gas, usually to a pressure of about 12 atm., and regulator *e* was adjusted to give a downstream

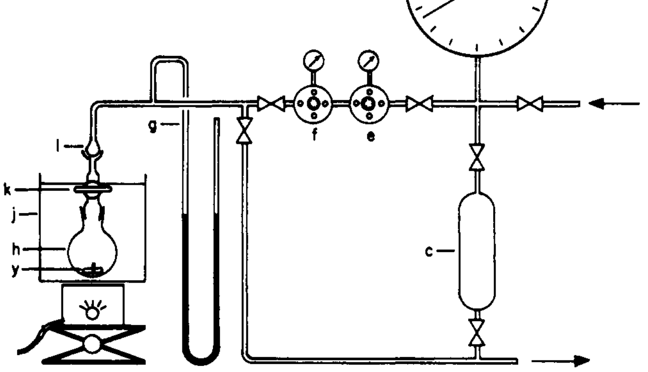

Figure 1. Apparatus for measuring solubilities by Method B

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[1] Deceased.

pressure of 1.35 atm. absolute. Regulator f was then adjusted to fill the apparatus as far as stopcock k to the desired pressure, taking into account the vapor pressure of the liquid. The pressure on gage d was measured to ±0.01 atm., and then stopcock k was opened. The pressure drop was recorded, and a compressibility factor applied in order to convert to ideality. The solubility of the gas in the liquid was calculated using the expression:

$$\text{Solubility } K \text{ (moles/liter)} = \frac{\rho_t}{0.4\ \rho_r}\left[\frac{(P_0f_0 - P_1f_1)\ V_1 \times 273.16}{22.414\ (273.16 + T)} - (V_2 - \frac{0.4\ \rho_r}{\rho_t})\ \frac{P_2}{22.414}\ (\frac{273.16}{273.16 + t})\right]$$

where ρ_t = density of solvent at bath temperature
ρ_r = density of solvent at 23° ± 1° C.
P_0 = initial gage reading, atm.
P_1 = final gage reading, atm.
P_2 = partial pressure of gas at bath temperature, atm.
f_0 = a factor for converting gas pressure to ideality at pressure P_0
f_1 = a factor for converting gas pressure to ideality at pressure P_1
T = temperature of bomb and gage, ° C.
t = bath temperature, ° C.
V_1 = volume of gas reservoir, liters
V_2 = volume of absorption vessel, liters

To check some of the larger solubility values by weighing, flask h containing the degassed solvent (400 ml.) was closed off by stopcock k, separated from the apparatus at ball joint l, and weighed on a torsion balance. After saturation of the solvent with the gas, the flask and contents were reweighed, the weight of dissolved gas being determined by difference.

Materials. Ethylene was polymerization grade (Monsanto) with a maximum of 0.15% impurities, chiefly ethane and methane. Ethane and propane were research grade (Matheson Co., LaPorte, Tex.), 99.90 and 99.99% pure, respectively. Hydrogen came from the Air Reduction Co., Houston, Tex., and had a minimum purity of 99.50%. 1,2-Dichloroethane was manufactured by the Monsanto Co., Texas City, and had a purity of 99.95%. The n-hexane was high purity material from the Phillips Petroleum Co., Borger, Tex., the maximum impurities being benzene (0.5%) and methylcyclopentane (0.5%). Toluene was Fisher spectrophotometric grade.

RESULTS AND DISCUSSION

The vapor pressures of the solvents were first measured to ensure that no extraneous volatile materials were present. The vapor pressure of 1,2-dichloroethane has not been published previously, and measurements were therefore made to provide the necessary data. The vapor pressures of 1,2-dichloroethane are shown in Table III along with the solubility data. The solubility data are shown in Tables I to III. In these determinations, Method A was the more accurate, chiefly because of better temperature control. Although the temperature was controlled to only ±0.2° C. in Method B, the results are in good agreement with those from Method A.

Our solubility data for ethylene in toluene confirm the data of Hannaert *et al.* (*4*), who disagree with data

Table I. Solubility of Ethylene in Toluene and n-Hexane

Temp., ° C.	P_g, Mm.	α_0	Gas Solubility, Mole/Liter at 1 Atm.	Method
		Toluene		
−23	760.0	6.894	0.311	B
−20	760.0	6.320	0.283	B
−10	222.6	5.310	0.237	A
	359.9	5.240	0.234	A
	475.6	5.270	0.235	A
0	243.3	4.450	0.199	A
	393.6	4.380	0.196	A
	520.1	4.400	0.196	A
	594.5	4.410	0.196	A
	765.0	4.412	0.197	B
	765.0	4.444	0.199	B[a]
+10	260.9	3.850	0.172	A
	422.6	3.770	0.168	A
+20	275.4	3.420	0.153	A
	445.6	3.360	0.150	A
+22	760.0	3.189	0.142	B
		n-Hexane		
−10	200.4	6.53	0.291	A
	346.9	6.35	0.284	A
	465.9	6.33	0.283	A
0	507.0	5.42	0.242	A
	571.4	5.34	0.239	A
+10	543.3	4.77	0.213	A
	611.9	4.70	0.210	A
20	570.2	4.35	0.194	A
	643.7	4.27	0.190	A

[a] Value determined by weighing.

Table II. Solubility of Ethane and Propane in Toluene

Temp., ° C.	P_g, Mm.	α_0	Gas Solubility, Moles/Liter at 1 Atm.	Method
		Ethane		
−20.0	759.0	6.499	0.290	B
0.0	754.0	4.760	0.212	B
0.0	760.0	4.805	0.214	B
24.8	760.0	3.254	0.145	B
		Propane		
−20.0	759	72.352	3.228	B
−20.0	759	71.164	3.175	B[a]
0	756	24.588	1.097	B
0	757	25.036	1.117	B
0	757	26.381	1.177	B[a]
21.7	740	10.086	0.450	B
23.4	740	10.124	0.452	B[a]
25.7	739	9.992	0.446	B

[a] Determined by weighing.

Table III. Solubility of Hydrogen in 1,2-Dichloroethane, *n*-Hexane, and Toluene by Method A and Vapor Pressures of 1,2-Dichloroethane

Temp., ° C.	α_0	Gas Solubility, Moles/Liter at 1 Atm.	Vapor Pressure of Solvent, Atm. $\times 10^{-2}$
	1, 2-Dichloroethane		
−10.0	0.0349	1.557	1.487
0	0.0390	1.739	2.776
10	0.0425	1.890	4.881
20	...	...	8.210
25	0.0502	2.239	10.513
	n-Hexane		
−10	0.0852	3.801	
0	0.0926	4.131	
10	0.0991	4.471	
20	0.104	4.640	
	Toluene		
−10	0.0485	2.164	
0	0.0537	2.396	
10	0.0569	2.538	
20	0.0607	2.708	

given by others (*1, 5*). It was this disagreement that led us to double-check our results by weighing, to leave no doubt that our values are correct to within $\pm 2\%$. Furthermore, our values for toluene fall between those for benzene (*6*) and xylene (*8*), as one might expect.

Our data for ethylene in *n*-hexane do not agree very closely with the literature values. McDaniel (*10*) reported a Bunsen coefficient for ethylene in *n*-hexane of 2.814 at 22° C. and 2.505 at 35° C. Rosenthal (*11*) reported a Bunsen coefficient of 2.83 for the same components at 35° C. Interpolation and extrapolation of our results give Bunsen coefficients of 4.2 at 22° and 3.9 at 35° C. McDaniel's data for ethylene in benzene (*10*) also seem to disagree with other literature values (*6*), however, which leads us to suspect the accuracy of his work.

The data presented here for the solubility of hydrogen in *n*-hexane at 25° C. are 20% lower than those obtained from extrapolation of data reported by Frolich (*3*) for pressures of 10 to 110 atm. at 25° C. The extrapolation may not be valid, however, for such a large pressure range.

The solubility of hydrogen in toluene has been measured by Ipatiev and Levina (*7*) at pressures of 50 to 300 atm., and by Cook (*2*) at 1 atm. If the high pressure results are extrapolated to 1 atm., these as well as Cook's results agree with ours to within 5%.

Previous studies by Kireev and Romanchuk (*9*) on the solubility of hydrogen in 1,2-dichloroethane at 0° C. produced solubility coefficients greater by a factor of 3 than those reported here. It is possible that they did not take surface adsorption into account, since their Bunsen coefficients are very close to those obtained by us before we made corrections for this. The good agreement of our results with those of Cook for hydrogen in toluene strengthens our belief that the data of Kireev and Romanchuk are in error.

The solubility of propane in toluene has been measured elsewhere (*4*) and is in close agreement with the results of this work.

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