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Some Solubility Data for Ethane in *n*-Hexane

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The solubility of ethane in *n*-hexane is reported for temperatures of 0–30°C. The data contradict some rather old existing literature reports for hexane but fall in line with other data for C_9–C_6 hydrocarbons.

We wish to report some solubility data for ethane in *n*-hexane at 0–30°C. The results contradict existing literature values for this system (*3*, *4*) but fall in line with results for *n*-nonane, *n*-octane, and *n*-heptane (*5*).

The solubility measurements were carried out in duplicate according to a recently described technique (*6*). In this method the amount of gas required to saturate a known volume of liquid at a known temperature and partial pressure of gas was determined. Determination was made by measuring the change of pressure of the gas in the reservoir (a 286.4-ml bomb) after the previously evacuated absorption vessel had been filled and the liquid in it had been saturated by the gas. The gas flow to the liquid was controlled by two diaphragm-type regulators (Fisher-Governor Co., Marshalltown, Iowa) set to give the desired final pressure above the liquid. The solvent (300 ml at 23°C) was degassed by pumping out at 10^{-4} mm Hg at liquid nitrogen temperature in a 500-ml flask before being saturated with ethane while being stirred by a magnetic stirring bar and held at the desired temperature. The pressure in the reservoir was measured by a Heise gage calibrated with a Model 145 Digital Pressure Gage from Texas Instruments Co. (Houston, Tex.). This gage in turn had been calibrated against NBS standards to ±0.002 psia. Solvent vapor pressure and gas partial pressure were measured with a mercury manometer, and solvent temperature was controlled by a 1-gal Cellosolve bath maintained to within ±0.1°C of the desired temperature.

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The solubility of the ethane in the *n*-hexane was calculated using the expression

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

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

Ethane was 99.9% pure research grade from Matheson Co. (La Porte, Tex.) and *n*-hexane was high-purity material from Phillips Petroleum Co. (Borger, Tex.), the maximum impurities being benzene (0.5%) and methylcyclopentane (0.5%). The purities were checked by gas chromatography on a 5-ft × $^3/_{16}$-in. column of Porasil B at 50°C using a hydrogen flame detector. The hexane was passed through 3A Molecular Sieves and dried over sodium ribbon under argon before being degassed for use.

The results were confirmed to within ±2% by an additional gas chromatographic method. In this, a known quantity of ethane was equilibrated with the solvent in a vessel of known volume at a given temperature and pressure. An assay for ethane in the gas phase was then made by injecting samples into a helium flow of 45 ml/min passing through the above-mentioned column of Porasil B at 33°C and comparing the height of the ethane peak with that from a known ethane–argon blend. This method was only intended as a rough but independent check of the solubility values obtained by the primary method. Values for α_0 from the primary method are given in Table I and are averages of two measurements. α_0 is the Bunsen coefficient (defined as the volume of gas converted to STP absorbed into unit volume of solvent at 1 atm partial pressure of gas at the temperature concerned).

Table I. Some Solubility Data for Ethane in *n*-Hexane

Temp, °C	Gas solubility by pressure-change method, mol/l. at 1 atm.	Av value for α_0	α_0 as measured by gas chromatography
0	0.381 ± 0.006	8.54 ± 0.13	8.68
10	0.317 ± 0.010	7.10 ± 0.22	7.14
20	0.264 ± 0.005	5.89 ± 0.11	5.68
25	0.247 ± 0.005	5.54 ± 0.11	. . .
30	0.225 ± 0.012	5.04 ± 0.27	4.96

Table II. Solubilities of Ethane in Linear C_6–C_9 Hydrocarbons at +25° and +30°C

Temp, °C	Solvent	α_0	Author
+25	*n*-Nonane	4.28	Thomsen and Gjaldbaek (*5*)
+25	*n*-Octane	4.71	Thomsen and Gjaldbaek (*5*)
+25	*n*-Heptane	5.12	Thomsen and Gjaldbaek (*5*)
+25	*n*-Hexane	5.62	Thomsen and Gjaldbaek (*5*) extrapolated
+25	*n*-Hexane	5.54	This work
+30	*n*-Hexane	5.04	This work
+30	*n*-Hexane	2.87	McDaniel and Rosenthal (*3, 4*)[a]

[a] Believed by us to be erroneous.

The results from primary measurements varied generally by ±3% or less, an exception being the measurements at 30°C which showed variations of ±5%. The average values from the primary results differed from those from the chromatographic method by 3.5% or less.

The α_0 value for ethane in *n*-hexane at 30°C has been reported by McDaniel (*3*) to be 2.8680 which is only 57% of our measured value. Possible reasons for errors in McDaniel's work could be (a) he synthesized his own gases which might not have been pure, (b) his technique of eliminating consideration of solvent vapor pressure was not valid, or (c) he made an error in determining the volume of his apparatus. It is curious that results of Rosenthal for ethane in *n*-hexane and *n*-heptane (*4*) agree with those of McDaniel to three places of decimals and yet both sets of results contradict ours for ethane in *n*-hexane and those of Thomsen and Gjaldbaek (*5*) for ethane in *n*-heptane. The work of McDaniel and Rosenthal is made even more suspect on the basis of their results for ethylene in toluene which disagree with ours, and by the work on ethylene in benzene which disagrees with that of Horiuti (*2*).

We graphically extrapolated the solubilities given by Thomsen and Gjaldbaek for ethane in *n*-nonane, *n*-octane, and *n*-heptane at +25°C (Table II). A plot of α_0 vs. the number of carbons is almost linear and appears to predict a value of 5.5 for *n*-hexane at this temperature. Later we tried to find a simple mathematical dependency based on the number of carbon atoms in the solvent and found that the data conform to the relationship

$$\alpha_0 = 0.015\,n^2 - 0.665\,n + 9.07 \quad (n = \text{the number of carbon atoms in the solvent molecule})$$

When $n = 6$, α_0 becomes 5.62 (both extrapolated values being close to our value of 5.54 at this temperature). Considering the other several contradictions of McDaniel's and Rosenthal's data in the literature (*2, 5, 6*), we have little doubt that they are erroneous. Our results for ethane in *n*-hexane are therefore a correction of their data.

Considering that the solubilities of ethane in higher *n*-alkanes were not accurately predicted by the Hildebrand-Scott equation (*1*), we offer no correlation of our results with theory using analogous solubility parameters for *n*-hexane.

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