Henry's Constants for Methane, Ethane, Ethylene, Propane, and Propylene in Octadecane, Eicosane, and Docosane

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Henry's constants determined from chromatographic measurements are reported for five gases in three solvents in the temperature region 30° to 200° C.

THERMODYNAMIC properties of dilute solutions can frequently be measured by gas chromatography. Use of this technique was originally suggested by Martin (*6*). Since that time, its validity has been verified experimentally and theoretically by a number of workers (*1, 2, 3, 4, 5, 7*). This work reports low-pressure solubilities of five light hydrocarbons in three heavy paraffin solvents in the temperature region 30° to 200° C. While solubility data are relatively plentiful near room temperature, such data tend to be rare at temperatures well removed from 25° C. The results reported here may be of interest in petroleum refining and related operations.

EXPERIMENTAL

Measurements were made with a modified Wilkins Model 1520 Aerograph gas chromatograph. Acid-washed diatomaceous earth material (Chromosorb P) of mesh number 100/120 was used as solid support. The 20-foot columns consisted of coiled ¼-inch stainless steel pipe. A schematic diagram of the equipment is shown in Figure 1.

The solutes—methane, ethane, ethylene, propane, and propylene—were obtained from the Matheson Co. Reported purities exceeded 99%. Solvents with the following reported melting points (° C.) were obtained from Matheson, Coleman & Bell: octadecane, 27–28.5°; eicosane, 35–36.5°; and docosane, 43–45°. Helium was used as carrier gas; the flow rate was maintained at about 25 cc. per minute and accurately measured with a bubble flow meter.

Prior to loading the columns, solvent and solid support were weighed separately. Chloroform was added to dissolve the solvent and then slowly evaporated to allow uniform coating of the solid support. Columns were weighed before insertion in the chromatograph and again after runs were completed to determine any (very small) loss of solvent. Solute and air gas samples injected into the chromatograph had a volume of approximately 2 μl. each. The thermal-conductivity detector signal was recorded on a strip-chart Honeywell Electronik 15 recorder. Temperature in the chromatograph oven was controlled to within ± 0.1° C. by a Hallikainen Thermotrol.

DATA REDUCTION

Henry's constant H_i for solute i in a particular solvent is defined by

$$H_i = \frac{p_i}{x_i} \tag{1}$$

where p_i is the partial pressure of solute i, and x_i is its mole fraction. Henry's constant may be obtained from the chromatographic partition coefficient (*6*) according to

$$H_i = \frac{RT}{\beta M} \tag{2}$$

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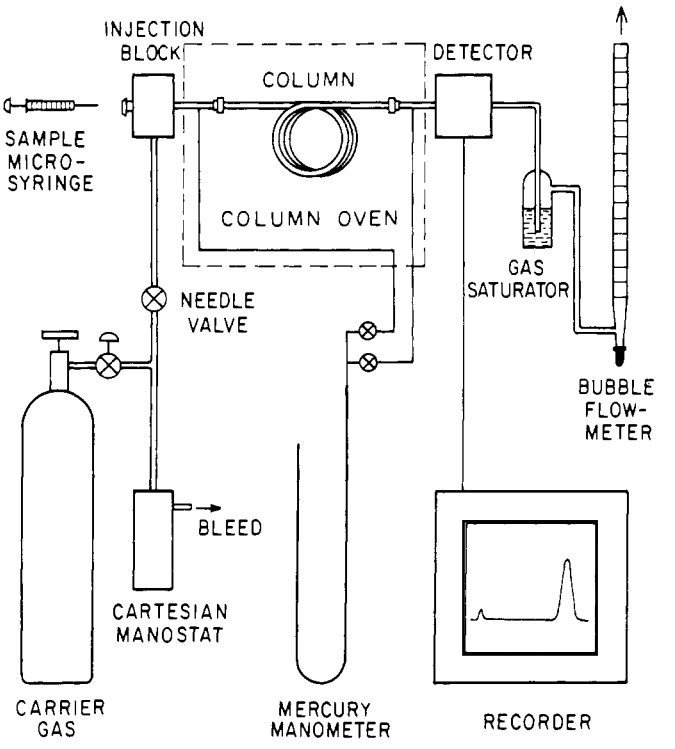

Figure 1. Gas chromatographic apparatus

where T is the column temperature, R is the gas constant, and M is the molecular weight of the solvent.

The partition coefficient, β, is defined as the ratio of the mass of solute per gram of solvent to the mass of solute per cc. of gas at column temperature. For a given system, β is related to peak retention time, t_R, by

$$\beta = \frac{(t_R - t_M)\, j\, V_o}{W} \tag{3}$$

where t_M is the peak retention time of an essentially insoluble gas (air), sec.; V_o is the flow rate of carrier gas at column outlet pressure and temperature, cc. per sec.; and W is the weight of solvent in column, grams.

The pressure-correction factor, j, is given by

$$j = \frac{1.5\,(P_{in}^2/P_{out}^2 - 1)}{P_{in}^3/P_{out}^3 - 1} \tag{4}$$

where P_{in} is the pressure at inlet of column and P_{out} is the pressure at outlet of column.

The partial molar enthalpy of solution is found from

$$\Delta\bar{h}_i = \bar{h}_i^L - h_i^g = R\,\frac{d \ln H_i}{d\, 1/T} \tag{5}$$

Table I. Henry's Constants, Atm.

Solvent	T, °C.	Methane	Ethane	Propane	Ethylene	Propylene
Octadecane	35	209	27.3	8.0	42.5	9.2
$C_{18}H_{38}$	50	239	33.5	10.7	50.6	12.1
	70	272	43.4	15.1	61.8	16.9
	90	255	54.0	20.6	74.4	22.7
	100	306	58.1	23.1	81.8	25.5
	150	395	86.4	39.2	114	42.6
Eicosane	50	226	33.1	10.6	50.5	12.1
$C_{20}H_{42}$	70	...	42.2	14.9	61.9	16.9
	100	286	56.9	22.9	79.8	25.3
	120	301	68.3	28.9	92.6	31.8
	140	356	79.8	36.3	106.4	39.3
Docosane	60	229	36.1	12.3	53.6	13.9
$C_{22}H_{46}$	110	269	60.2	24.9	82.6	27.5
	135	314	75.1	33.6	99.6	36.6
	160	338	86.2	44.0	112.7	44.2
	180	355	98.5	48.9	128	52.5
	200	411	115.0	60.5	147	64.7

where $\bar{h}_i^L$ is the partial molar enthalpy of i in dilute liquid solution and h_i^g is the molar enthalpy of pure gaseous i in the ideal-gas state at the same temperature.

RESULTS

Henry's constants for methane, ethane, ethylene, propane, and propylene in three solvents are given in Table I. Estimated uncertainties are about 3 to 5%, except for methane, where they are considerably larger, especially at the higher temperatures. The uncertainties are high for methane because of its small retention time. Further, Equation 3 assumes that the solubility of the "insoluble" gas is negligible compared to that of the solute gas; this assumption is least accurate for methane. Since hydrogen is less soluble than air, hydrogen was used as the "insoluble" gas in some of the experiments with methane. However, no essential difference was detected between the results using air and those using hydrogen.

Figure 2 shows the variation of Henry's constant with reciprocal temperature for the five gases in docosane. Straight lines were also obtained for similar plots of Henry's constants in octadecane and in eicosane. The slopes of the lines showed no significant variation among the three solvents. The partial molar enthalpies of solution are

	$\Delta\bar{h}_i$, kcal. per gram mole
Methane	−1.27
Ethane	−2.58
Ethylene	−2.21
Propane	−3.59
Propylene	−3.43

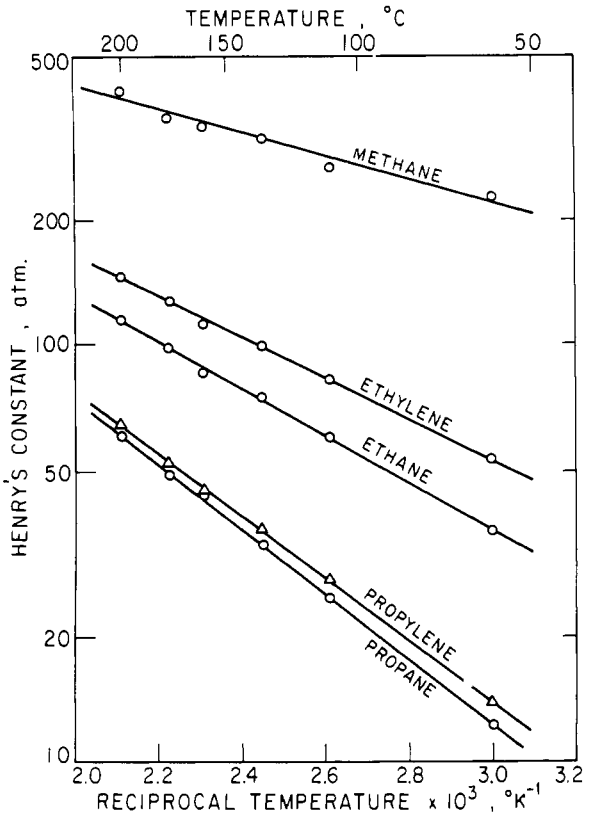

Figure 2. Henry's constants in docosane

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