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# Solubility of Carbon Dioxide, Methane, and Ethane in *n*-Octacosane

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**Solubility of carbon dioxide, methane, and ethane in *n*-octacosane has been measured in a semiflow apparatus over the temperature range of 100–300 °C and pressure from 10 to 50 atm. Henry's constant and partial molar volume at infinite dilution are determined from the solubility data.**

## Introduction

This article reports data from an investigation of gas solubilities in wax slurry for Fischer–Tropsch synthesis reactors. Solubility of carbon dioxide, methane, and ethane in *n*-octacosane ($n$-$C_{28}$) has been determined over the temperature range of 100–300 °C and pressure from 10 to 50 atm. Henry's constant and partial molar volume at infinite dilution of the dissolved gases are obtained by fitting the Krichevsky–Kasarnovsky equation to the data.

## Experimental Section

A semiflow apparatus has been designed and constructed for the measurement of gas solubilities in molten waxes. Detailed description of the equipment and operation procedure has been reported (*1*). In the course of an experiment, the molten wax was kept in a presaturator and an equilibrium cell, which were housed in series in a thermostated nitrogen bath. A gas stream continuously sparged through the cells. Upon saturation, liquid samples from the equilibrium cell were withdrawn, reduced in pressure, and collected in a trap. The condensed wax was weighed with an analytical balance, and the liberated gas from the trap was measured volumetrically in a buret. The temperature of the equilibrium cell contents was measured to ±0.1 °C by a calibrated type K chromel–alumel thermocouple. Pressure was measured by a Heise gauge to ±0.05 atm.

The gases were purchased from Matheson Gas Products with a minimum purity of 99.8% for carbon dioxide and 99% for methane and ethane. The *n*-octacosane was purchased from Alfa Products, Morton Thiokol, Inc., with a minimum purity of 99%.

Possible thermal degradation of the wax during the experiment was examined by gas chromatographic (GC) analysis of the wax and by comparing repeated data points. The GC patterns of fresh and used waxes did not show any differences, and solubility data were reproducible within experimental errors regardless of the age of wax in operation.

## Results and Discussion

Tables I, II, and III present the solubility, $x$, in mole fraction, of carbon dioxide, methane, and ethane in *n*-octacosane of this work. Because of the low volatility of *n*-octacosane, the equilibrium gas phase is virtually pure solute at 100 and 200 °C where the gas composition, $y$, in mole fraction, is not explicitly reported. The gas composition measured at 300 °C is reported

**Table I. Carbon Dioxide (CD) + *n*-Octacosane VLE Data**

| $t$, °C | $P$, atm | $x_{CD}$ | $y_{CD}$ | $K_{CD}$ |
|---|---|---|---|---|
| 100.2 | 10.05 | 0.102 | | 9.84 |
| | 20.14 | 0.184 | | 5.44 |
| | 30.01 | 0.254 | | 3.93 |
| | 40.15 | 0.324 | | 3.09 |
| | 49.90 | 0.379 | | 2.64 |
| 200.3 | 9.87 | 0.0688 | | 14.5 |
| | 20.04 | 0.135 | | 7.39 |
| | 30.18 | 0.194 | | 5.14 |
| | 39.89 | 0.247 | | 4.05 |
| | 49.95 | 0.293 | | 3.42 |
| 300.3 | 9.81 | 0.0596 | 0.9957 | 16.7 |
| | 20.06 | 0.122 | 0.9975 | 8.16 |
| | 30.08 | 0.176 | 0.9981 | 5.69 |
| | 39.92 | 0.226 | 0.9983 | 4.42 |
| | 49.91 | 0.270 | 0.9983 | 3.69 |

**Table II. Methane (M) + *n*-Octacosane VLE Data**

| $t$, °C | $P$, atm | $x_M$ | $y_M$ | $K_M$ |
|---|---|---|---|---|
| 100.1 | 9.77 | 0.0566 | | 17.7 |
| | 19.90 | 0.113 | | 8.87 |
| | 30.04 | 0.163 | | 6.13 |
| | 40.19 | 0.204 | | 4.90 |
| | 49.97 | 0.244 | | 4.11 |
| 200.2 | 9.78 | 0.0496 | | 20.2 |
| | 19.81 | 0.100 | | 10.00 |
| | 29.88 | 0.143 | | 6.99 |
| | 40.36 | 0.189 | | 5.30 |
| | 49.95 | 0.224 | | 4.46 |
| 300.1 | 9.48 | 0.0493 | 0.9962 | 20.2 |
| | 19.74 | 0.102 | 0.9979 | 9.78 |
| | 30.21 | 0.152 | 0.9985 | 6.57 |
| | 40.17 | 0.195 | 0.9986 | 5.12 |
| | 50.11 | 0.230 | 0.9986 | 4.34 |

**Table III. Ethane (E) + *n*-Octacosane VLE Data**

| $t$, °C | $P$, atm | $x_E$ | $y_E$ | $K_E$ |
|---|---|---|---|---|
| 100.1 | 9.76 | 0.180 | | 5.54 |
| | 19.90 | 0.322 | | 3.11 |
| | 28.82 | 0.425 | | 2.35 |
| | 40.18 | 0.504 | | 1.98 |
| 200.1 | 9.82 | 0.113 | | 8.85 |
| | 19.87 | 0.207 | | 4.83 |
| | 29.81 | 0.287 | | 3.48 |
| | 37.46 | 0.335 | | 2.99 |
| 300.0 | 9.62 | 0.0840 | 0.9957 | 11.9 |
| | 19.76 | 0.166 | 0.9973 | 6.00 |
| | 29.83 | 0.236 | 0.9976 | 4.24 |
| | 39.87 | 0.297 | 0.9977 | 3.36 |

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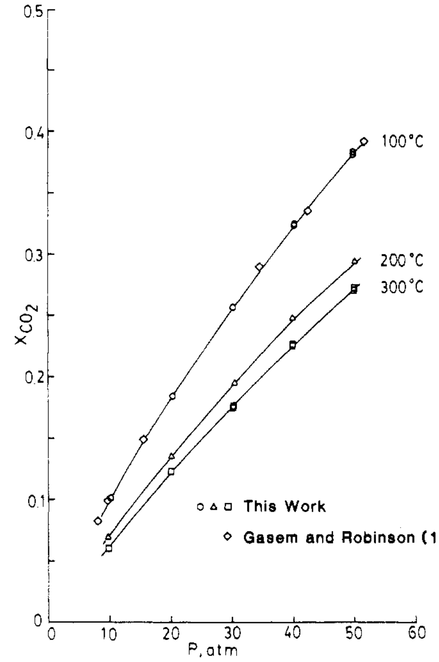


**Figure 1.** Solubility of carbon dioxide in *n*-octacosane.

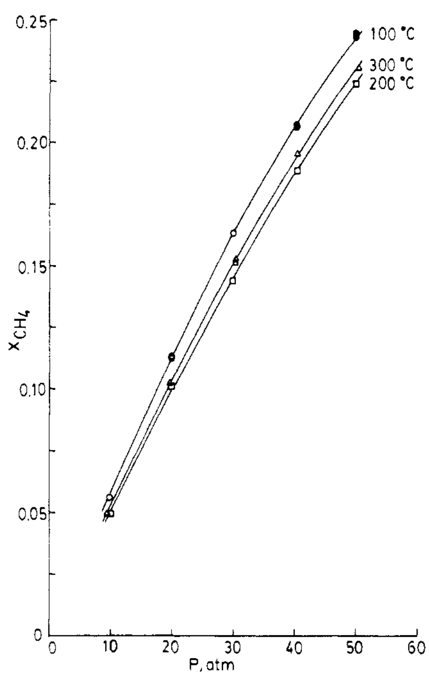


**Figure 2.** Solubility of methane in *n*-octacosane.

**Table IV. Henry's Constant and Partial Molar Volume at Infinite Dilution**

| solute | temp, °C | Henry's const, atm | partial molar vol, mL/mol |
|---|---|---|---|
| $CO_2$ | 100 | 94 (2)[a] | 115 (6)[a] |
| | 200 | 137 (1) | 133 (8) |
| | 300 | 156 (2) | 169 (10) |
| $CH_4$ | 100 | 163 (2) | 125 (13) |
| | 200 | 189 (2) | 141 (14) |
| | 300 | 183 (3) | 152 (24) |
| $C_2H_6$ | 100 | 48 (1) | 274 (22) |
| | 200 | 80 (1) | 289 (15) |
| | 300 | 107 (1) | 261 (19) |

[a] Numbers in parentheses are the standard deviations.

in Tables I, II, and III. The reported data are the average values of at least four replicate samples at each condition of temperature and pressure. The samples are generally repro-

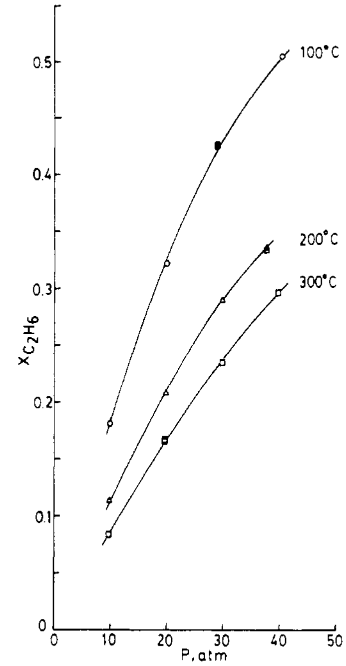


**Figure 3.** Solubility of ethane in *n*-octacosane.

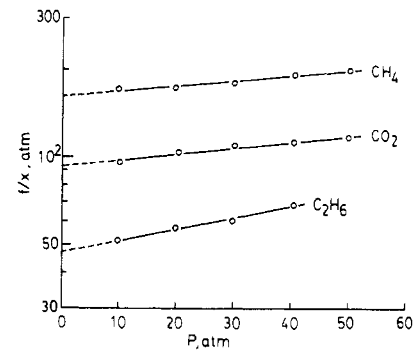


**Figure 4.** Plot of solute ($f/x$) versus pressure at 100 °C.

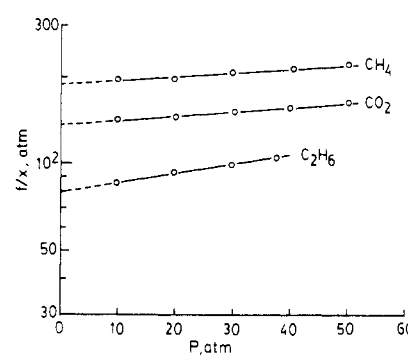


**Figure 5.** Plot of solute ($f/x$) versus pressure at 200 °C.

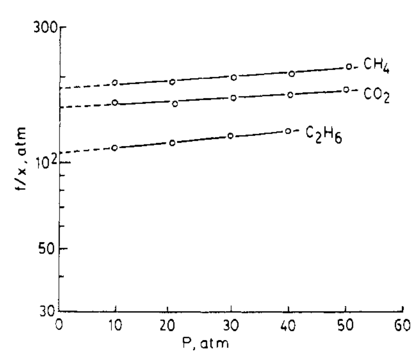


**Figure 6.** Plot of solute ($f/x$) versus pressure at 300 °C.

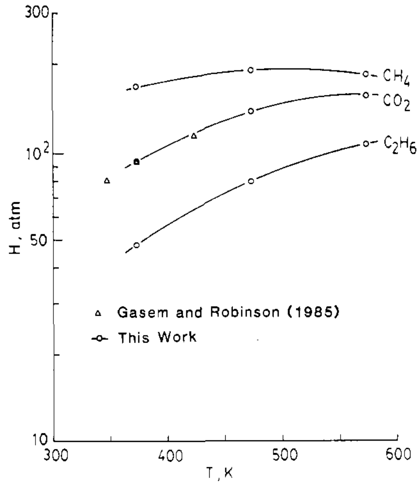


**Figure 7.** Henry's constant of carbon dioxide, methane, and ethane in *n*-octacosane.

ducible to within 1.5% in the mole fraction of the gas component. $K$ values of gases reported in the tables were calculated from the averaged values of $x$ and $y$ according to the definition, $K \equiv y/x$. Figures 1-3 show the gas solubility as a function of pressure at different temperatures. Individual data points are shown in the figures where they can be distinguished. For carbon dioxide and ethane, solubility decreases with increasing temperature at the conditions of this work. The solubility of methane passes through a minimum at a temperature between 100 and 300 °C. Solubility of carbon dioxide in *n*-octacosane reported by Gasem and Robinson (*2*) is shown in Figure 1 for comparison with our data. The agreement is excellent.

Figures 4-6 show ln $(f/x)$ of the solute as a function of pressure at a constant temperature. The solute fugacity $f$ is calculated from the equilibrium gas by using the generalized correlation of fugacity coefficient by Lee and Kesler (*3*). Linear isotherms are obtained with an average absolute deviation of 0.8%. By the equation of Krichevsky and Kasarnovsky (*4*) the intercept at the vapor pressure of the solvent determines the Henry's constant, and the slope gives the partial molar volume at infinite dilution. The values thus obtained are reported in Table IV. Henry's constant is subject to an uncertainty of about 2%. Partial molar volume at infinite dilution is less accurate; their estimated standard deviations are listed in Table IV. Figure 7 shows the Henry's constant as a function of temperature. Our results are in agreement with those reported by Gasem and Robinson for $CO_2$ mixtures.

**Registry No.** $CO_2$, 124-38-9; $CH_4$, 74-82-8; $C_2H_6$, 74-84-0; *n*-octacosane, 630-02-4.

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# Solubility of Carbon Dioxide, Methane, and Ethane in *n*-Eicosane

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**Solubility of carbon dioxide, methane, and ethane in *n*-eicosane has been measured in a semiflow apparatus at temperatures up to 300 °C and pressures to 50 atm. Henry's constant of the dissolved gases in *n*-eicosane is determined from the data.**

### Introduction

This article reports data from an investigation of gas solubilities in model compounds of wax slurry of Fischer-Tropsch synthesis reactors. Solubility of carbon dioxide, methane, and ethane in *n*-eicosane at temperatures up to 300 °C and pressures to 50 atm has been determined, and Henry's constant is obtained from the data. The results are compared with literature values.

### Experimental Section

A semiflow apparatus has been designed and constructed for the measurements of gas solubility in molten waxes. Detailed description of the equipment and sampling procedure has been reported (*1*). In the course of an experiment, molten wax was kept in a presaturator and in an equilibrium cell. A stream of gas passed through the cells in series. Upon saturation, samples from the equilibrium cell were withdrawn, reduced in pressure, and collected in a trap. The collected wax was weighed with an analytical balance, and the liberated gas from the trap was measured volumetrically in a buret. Temperature of the equilibrium cell was measured to an accuracy of ±0.1 °C by a type K chromel-alumel thermocouple inserted in the cell which is housed in a thermostated bath. The pressure was measured by a Heise gauge to ±0.05 atm.

The gases were purchased from Matheson Gas Products with a minimum purity of 99.0% for methane and ethane, and 99.8% for carbon dioxide. *n*-Eicosane was purchased from Aldrich Chemical Co., Inc., with a stated minimum purity of 99%. Possible thermal degradation of *n*-eicosane was examined by gas chromatographic (GC) analysis. No degradation was observed.

### Results and Discussion

Table I presents vapor-liquid equilibrium (VLE) data for carbon dioxide + *n*-eicosane at four temperatures: 50.1, 100.3, 200.0, and 300.2 °C. Table II presents the VLE data of methane + *n*-eicosane at three temperatures: 100.2, 200.3, and 300.0 °C. Table III presents the VLE data of ethane + *n*-eicosane at three temperatures: 100.6, 200.5, and 299.7 °C. At each temperture, data are reported at five pressures 10, 20, 30, 40, and 50 atm for carbon dioxide and methane. Since the vapor pressure of ethane in the source cylinder was below 50 atm, the solubility of ethane was determined at only four pressures 10, 20, 30, and 40 atm.

 