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

Fuan-Nan Tsai,[†] Stanley H. Huang, Ho-Mu Lin, and Kwang-Chu Chao*

School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907

The solubility of methane, ethane, and carbon dioxide in *n*-hexatriacontane has been measured experimentally by using a semiflow vapor-liquid equilibrium apparatus. For each gas, isotherms at 100, 200, and 300 °C were measured, each at five pressures: 10, 20, 30, 40, and 50 atm. Henry's constant and partial molar volume at infinite dilution are evaluated from the data.

Introduction

The solubility of methane, ethane, and carbon dioxide in heavy paraffins is of interest in some industrial processes, notably Fischer-Tropsch syntheses. Gasem and Robinson (*1*) reported solubility of carbon dioxide in several heavy n-paraffins at temperatures to 150 °C. Data are not available on solubility of methane, ethane, and carbon dioxide in very heavy n-paraffins at high temperatures and pressures.

In this work we use a semiflow apparatus to determine the solubility of methane, ethane, and carbon dioxide in *n*-hexatriacontane (n-$C_{36}H_{74}$) at three temperatures, 100, 200, and 300 °C, and pressures to 50 atm.

Experimental Section

A semiflow vapor-liquid equilibrium apparatus is used for the measurement of gas solubility in this work. The apparatus and procedure have been described (*2*). Briefly, a gas stream from a high-pressure cylinder is passed through two cells in series containing the hydrocarbon liquid. The first cell is the presaturator and the second the equilibrium cell. Saturated liquid from the latter is withdrawn, released under pressure, and collected in a trap. The volume of the liberated gas is measured in a buret. The mass of the collected hydrocarbon is determined by weighing the trap. The temperature of the equilibrium cell housed in a thermostated box is measured to ±0.1 °C. Pressure is determined to ±0.05 atm with a Heise Bourdon gauge.

The sources and purities of chemicals used in this work are given as follows (chemical, supplier, purity (%): CH_4, Matheson, 99+; C_2H_6, Matheson, 99+; CO_2, Matheson, 99.8+; n-C_{36}, Alfa, 99. No further purification of the chemicals was attempted.

In this work gas solubility measurement has been completed for methane, ethane, and carbon dioxide in *n*-hexatriacontane at three temperatures (100, 200, and 300 °C). Along each isotherm, five pressures (10, 20, 30, 40, and 50 atm) were investigated for methane and carbon dioxide and four pressures (10, 20, 30, and 40 atm) for ethane. The measurement at each temperature was carried out in the sequence 30, 50, 40, 20, and 10 atm in order to reveal any possible supersaturation or undersaturation. No such effects were detected.

Table I. Solubility Data of Methane, Ethane, and Carbon Dioxide in *n*-Hexatriacontane

temp, °C	press., atm	solute mole fraction
	CH_4	
100	10.11	0.0673
	20.07	0.130
	30.03	0.182
	40.06	0.230
	49.94	0.271
200	10.06	0.0605
	20.02	0.118
	30.06	0.171
	39.93	0.211
	49.93	0.255
300	10.08	0.0587
	20.12	0.114
	30.03	0.166
	40.08	0.212
	50.05	0.250
	C_2H_6	
100	10.07	0.212
	20.01	0.362
	30.00	0.466
	39.80	0.532
199.9	10.01	0.126
	20.04	0.234
	29.98	0.321
	39.96	0.390
299.9	10.06	0.101
	20.07	0.190
	30.00	0.263
	39.99	0.327
	CO_2	
100.0	10.08	0.110
	20.10	0.209
	29.97	0.289
	39.99	0.357
	49.99	0.415
200.2	10.09	0.0803
	19.75	0.155
	29.95	0.220
	39.90	0.274
	49.92	0.324
300.1	10.06	0.0707
	19.94	0.138
	29.97	0.198
	40.03	0.250
	50.00	0.297

Table II. Henry's Constant and Partial Molar Volume of Methane, Ethane, and Carbon Dioxide in *n*-Hexatriacontane

solute	temp, °C	Henry's const, atm	infinite diln partial mol vol, mL/mol
CH_4	100.0	141	142
	200.0	157	166
	300.0	164	180
C_2H_6	100.0	40.9	348
	199.9	72.6	306
	299.9	92.5	298
CO_2	100.0	84.3	143
	200.2	117	175
	300.1	134	189

[†] Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan.

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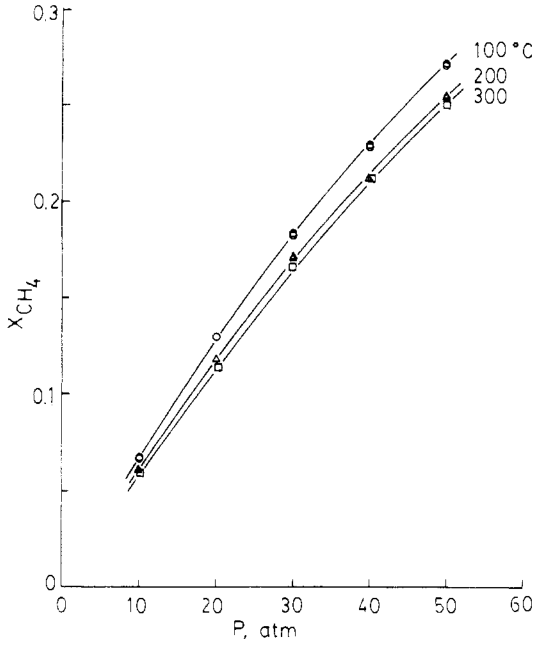

Figure 1. Solubility of methane in *n*-hexatriacontane.

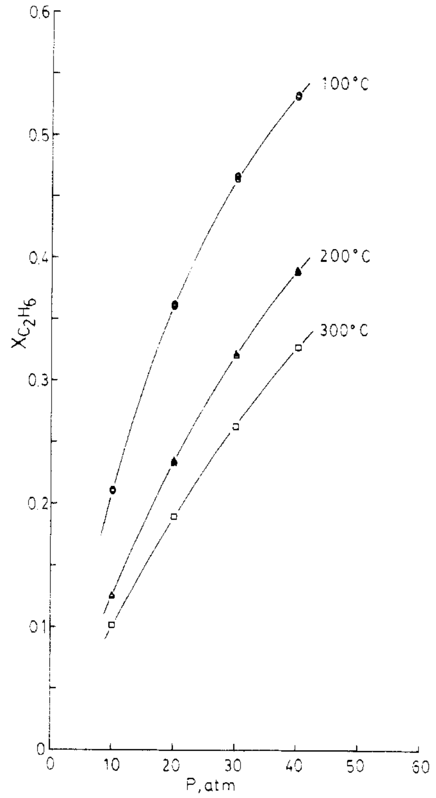

Figure 2. Solubility of ethane in *n*-hexatriacontane.

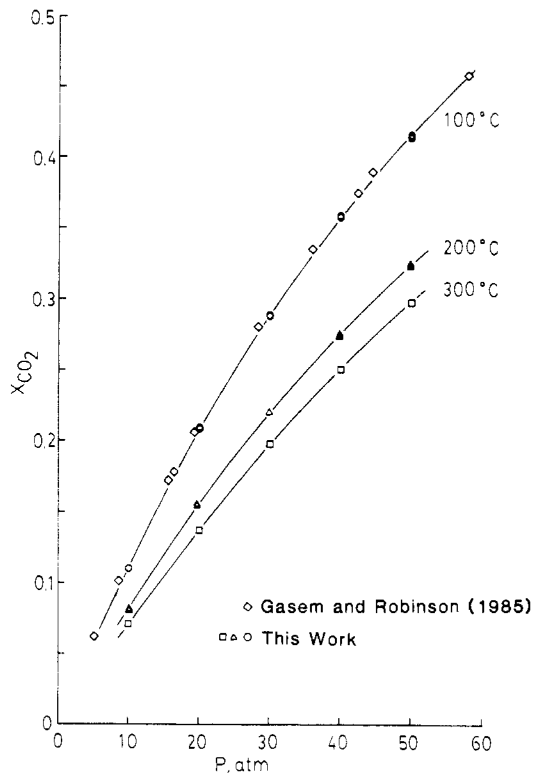

Figure 3. Solubility of carbon dioxide in *n*-hexatriacontane.

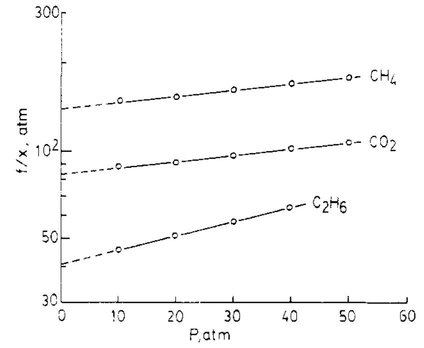

Figure 4. Plot of ln (f/x) vs. p at 100 °C.

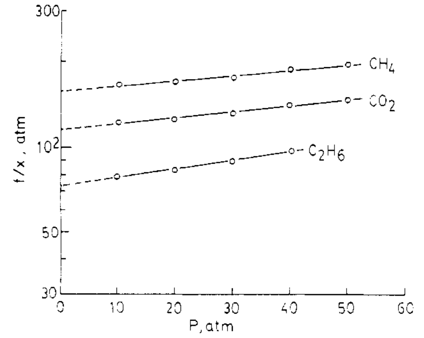

Figure 5. Plot of ln (f/x) vs. p at 200 °C.

Results and Discussion

Table I presents the solubility data of methane, ethane, and carbon dioxide in *n*-hexatriacontane of this work. The volatility of *n*-hexatriacontane is extremely low, and the equilibrium gas is found to be almost pure solute at all conditions studied though no gas composition is explicitly reported. At least four replicate measurements were conducted at each condition of tempera-

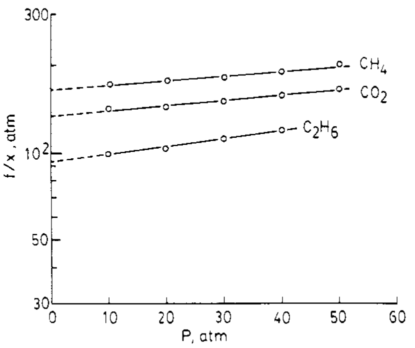

Figure 6. Plot of ln (f/x) vs. p at 300 °C.

ture and pressure. The multiple solubility data are generally reproducible to within 1.5% in mole fraction of the dissolved solute. Individual measurements are shown in Figures 1-3 as separate points where they can be distinguished. The observed gas solubilities increase with increasing pressure and decreasing temperature.

In Figure 3 we include the carbon dioxide solubility data of Gasem and Robinson (*1*) at 100 °C for comparison. The agreement of their data and ours seems reasonable with our data being a shade lower, the largest difference amounting to 2.5%.

Henry's constant and partial molar volume at infinite dilution are determined from the solubility data by plotting ln (f/x) of the solute at a temperature as a function of pressure. The fugacity f is calculated for the pure solute gas by using the Lee-Kesler correlation (*3*). Figures 4-6 show the linear result that is obtained. By the equation of Krichevsky and Kasarnovsky (*4*), the intercept at pressure (p) equal to the vapor pressure of the solvent determines Henry's constant, and the slope gives the partial molar volume at infinite dilution. Table II presents the results. The Henry's constant values are estimated to be uncertain to about 3%; the partial molar volume values to about 10%. Figure 7 shows Henry's constant as a function of temperature. Our results agree well with those of Gasem and Robinson for CO$_2$ mixtures.

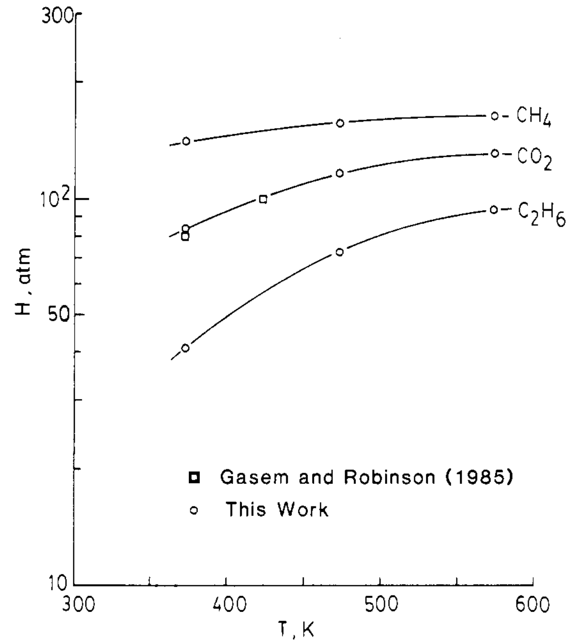

Figure 7. Henry's constant of methane, ethane, and carbon dioxide in n-hexatriacontane.

Registry No. CO$_2$, 124-38-9; CH$_4$, 74-82-8; C$_2$H$_6$, 74-84-0; hexatriacontane, 630-06-8.

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High-Pressure Specific Heat Capacities of Pure Water and Seawater

Chen-Tung A. Chen

Institute of Marine Geology, Sun Yat-Sen University, Kaohsiung, Taiwan, 80424, Republic of China

Equations of state for pure water and seawater were used to calculate high-pressure specific heat capacities at constant pressure (C_p) and at constant volume (C_v). Equations are given for pure water C_p and C_v values over the temperature range of 0-100 °C and pressure range of 0-1000 bar. Equations are also given for seawater C_p and C_v values over the salinity range of 0-40, temperature range of 0-40 °C, and pressure range of 0-1000 bar. These equations agree with the direct measurements reported in the literature for pure water to within ±0.026% over the measurement ranges of 20-100 °C up to 500 bar. No direct-pressure seawater measurements are available for comparison.

Introduction

Among the thermodynamic properties of pure water and seawater, the specific heat capacity is of primary importance. For instance, if two water masses of differing salinity and temperature are mixed uniformly, the resultant temperature and density are a function of heat capacity. Also, heat capacity data are needed for estimating the heat storage capacity of the oceans, for converting sound speeds to isothermal compressibilities, and for computing the adiabatic temperature gradient and static stability of waters. The data are also used in the investigation of structural changes of water.

Several pure water and seawater heat capacity measurements have been made at 1 atm (*1-6*). Because of experimental difficulties, however, no direct measurement has yet

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