DOE/PC/70024--T14

DE88 008541

Technical Progress Report
to
U.S. Department of Energy
Pittsburgh Energy Technology Center

Contract No. DE-AC22-84PC70024
on
Synthesis Gas Solubility in
Fischer-Tropsch Slurry

K.C. Chao
Principal Investigator

School of Chemical Engineering
Purdue University
West Lafayette, IN 47907

Progress Period: 1/1/86 - 3/31/86

Table of Contents

Summary

This is the quarterly progress report for the first quarter of 1986, January through March, on Synthesis Gas Solubility in Fischer-Tropsch Slurry.

Experimental determination of solubility of CO in two n-paraffin solvents was completed in this quarter. We present the solubility data that we have determined for five gases in two paraffin solvents in ten tables.

The solubility data have been correlated with three cubic equations of state employing van der Waals quadratic mixing rules. The correlation development is being continued.

Preparation has been made to measure solubility of mixed H_2/CO gas in n-paraffin solvents.

Gas Solubility Data

In the first quarter of 1986, January-March, we completed the measurement of solubility of CO in n-eicosane and in n-octacosane. The experimental measurement was started as soon as the solubility apparatus was moved into the new fume hood. Solubility was determined at three temperatures (100, 200, and 300°C) and five pressures (10, 20, 30, 40, and 50 atm) which combine to define 15 states of temperature and pressure for each solute-solvent pair. Figures 1 and 2 show the results.

Now a total of five gases (hydrogen, methane, ethane, carbon dioxide, and carbon monoxide) have been measured in their solubilities in the two high n-paraffin solvents. The same 15 states of temperature and pressure were studied for all the 10 solute-solvent pairs except for ethane for which the highest pressure of 50 atm was not attained.

We present the vapor-liquid equilibrium VLE data in tables as follows:

Table 1. Hydrogen + n-eicosane VLE data

Table 2. Hydrogen + n-octacocane VLE DATA

Table 3. Carbon monoxide + n-eicosane VLE data

Table 4. Carbon monoxide + n-octacocane VLE data

Table 5. Methane + n-eicosane VLE data

Table 6. Methane + n-octacocane VLE data

Table 7. Carbon dioxide + n-eicosane VLE data

Table 8. Carbon dioxide + n-octacocane VLE data

Table 9. Ethane + n-eicosane VLE data

Table 10. Ethane + n-octacocane VLE data

The solubility data have been correlated with Krichevsky-Kasarnovsky equation. Figure 3 shows the correlation at 100°C; Figure 4 at 200°C; and Figure 5 at 300°C. The pressure dependence of ln (f/x) has been found to be linear for the data of this work.

Henry's constant has been determined as the intercept of the correlated (f/x) at zero value of $(p-p_2^{sat})$. Figure 6 shows the Henry's constants in n-eicosane; and Figure 7 shows the constants in n-octacosane. Data from the literature are included in the figure for comparison. Table 11 presents the values of the constants. Henry's constant has been reported in the literature for several gases in a number of high n-paraffins at 150°C. We interpolate our results to 150°C and show them in Figure 8 for comparison with the values in the literature. Excellent agreement is obtained of our results with most literature values. Only two points from the literature appear to fall off.

Figure 8 is important in showing the significant dependence of the Henry's constant on the carbon number of the n-paraffin molecule. Solubility of a gas in a n-paraffin changes with the carbon number of the paraffin. It is imperative in correlation development to be able to describe the variation with molecular weight (or carbon number). It seems quite necessary to test any correlations that will be developed with solubility data in Fischer-Tropsch waxes since the waxes are made up of n-paraffins molecules of varying carbon numbers.

Correlation of Data

We have started correlation of the solubility data, and have fitted equations of state to the data. The Soave equation, Peng-Robinson equation, and the Cubic Chain-of- Rotators equation have been examined with the use of vand der Waal's classical quadratic mixing rules.

$$\Theta_m = \sum_i \sum_j x_i x_j \Theta_{ij}$$

where Θ is an equation constant: a, b, or c. The cross-interaction constants are expressed as follows:

$$a_{ij} = (1-k_{aij})(a_i a_j)^{0.5}$$

$$b_{ij} = (1-k_{bij})(b_i+b_j)/2$$

$$c_{ij} = (1-k_{cij})(c_i+c_j)/2$$

Table 12 shows the correlation with the Redlich-Kwong-Soave equation. Three sets of calculations are reported. In the one parameter calculation k_b is set to be zero, and the parameter k_a is adjusted to fit data. In the second calculation both k_a and k_b are adjusted. In the third calculation the k_b value is set to be zero and k_a is expressed as a linear function of temperature,

$$k_a = k_{ao} + k_{a1}T$$

Table 13 shows the correlation with the Peng-Robinson equation. Three sets of calculations are reported and the calculations are similar to those described for the RKS equation.

Table 14 shows the correlation with the CCOR equation. Two sets of calculations are reported. In the first calculation parametes k_a and k_c are adjusted and are assigned constant values for each solute-solvent pair. In the second calculation k_c is held constant, but k_a is expressed as a linear function of temperature.

Good fitting of the data is obtained in most of the calculations. For each equation the last set of calculation turns out to be the best, and the last set of calculations of the CCOR equation appears to be the best of all.

In spite of the good fitting of the data, the interaction constants show large variation from eicosane to octacosane. In view of the sensitive dependence of the calculation on the interaction constants, the observed large variation of the interaction constants from eicosane to octacosane is an indication of the inadequacy of the model to decribe the dependence of the solubility on the molecular weight of the solvent. We are continuing the correlation development.

Preparation for Measurement of H_2/CO_2 Mixtures

We have just about completed the prepartion for the experimental determination of solubility of $H_2 + CO$ gas mixture. Gas mixture Primary Standards were obtained from Matheson Gas Products, Inc. at hydrogen concentrations of approximately 20, 30, 40, and 50 mol %, and calibration of a Carle Analytical gas chromatograph has been completed. The Carle GC is equipped with a heated vanadium tube for the separation of hydrogen by permeation.

Table 1 Hydrogen + n-Eicosane VLE Data

T, K	P, atm	x_H	y_H
373.4	9.96	0.01133	1.0
373.4	19.87	0.02287	1.0
373.4	30.04	0.03476	1.0
373.4	40.24	0.04642	1.0
373.4	50.15	0.05629	1.0
473.6	9.89	0.01818	0.9985
473.6	19.90	0.03616	0.9992
473.6	30.04	0.05393	0.9994
473.6	39.83	0.07152	0.9995
473.6	49.69	0.08662	0.9996
573.3	9.81	0.02414	0.9617
573.3	19.89	0.05013	0.9815
573.3	29.93	0.07416	0.9878
573.3	40.04	0.09649	0.9911
573.3	49.99	0.1169	0.9926

Table 2 Hydrogen + n-Octacosane VLE Data

T, K	P, atm	x_H	y_H
373.3	9.73	0.01488	1.0
373.3	19.87	0.02955	1.0
373.3	30.05	0.04280	1.0
373.3	40.29	0.05965	1.0
373.3	49.88	0.07149	1.0
473.3	10.01	0.02063	1.0
473.3	19.75	0.03979	1.0
473.3	30.01	0.05971	1.0
473.3	39.97	0.07999	1.0
473.3	50.01	0.09932	1.0
573.2	10.04	0.02877	0.9965
573.2	19.83	0.05773	0.9982
573.2	30.08	0.08573	0.9988
573.2	40.03	0.1104	0.9991
573.2	50.04	0.1371	0.9993

Table 3 Carbon Monoxide + n-Eicosane VLE Data

T, K	P, atm	X_{CM}	Y_{CM}
373.4	10.07	0.01867	1.0
373.4	19.77	0.03800	1.0
373.4	30.07	0.05712	1.0
373.4	40.28	0.07614	1.0
373.4	49.97	0.09218	1.0
473.5	9.89	0.02303	1.0
473.5	19.78	0.04689	1.0
473.5	29.91	0.07080	1.0
473.5	40.16	0.09485	1.0
473.5	49.90	0.1166	1.0
573.2	9.94	0.02891	1.0
573.2	19.84	0.05862	1.0
573.2	29.89	0.08906	1.0
573.2	40.25	0.1166	1.0
573.2	49.71	0.1393	1.0

Table 4 Carbon Monoxide + n-Octacosane VLE Data

T, K	P, atm	X_{CM}	Y_{CM}
373.5	9.95	0.02269	1.0
373.5	19.73	0.04524	1.0
373.5	29.98	0.06955	1.0
373.5	40.21	0.09155	1.0
373.5	50.03	0.1117	1.0
473.2	10.07	0.02745	1.0
473.2	19.65	0.05545	1.0
473.2	30.14	0.08295	1.0
473.2	39.92	0.1089	1.0
473.2	49.96	0.1307	1.0
573.5	9.94	0.03361	1.0
573.5	19.74	0.06691	1.0
573.5	30.02	0.09931	1.0
573.5	40.18	0.1308	1.0
573.5	50.06	0.1557	1.0

Table 5 Methan + n-Eicosane VLE Data

T, k	P, atm	X_M	Y_M
373.4	9.95	0.04723	1.0
373.4	19.73	0.09029	1.0
373.4	29.78	0.1324	1.0
373.4	39.84	0.1719	1.0
373.4	49.85	0.2091	1.0
473.5	9.93	0.04266	0.9984
473.5	19.69	0.08447	0.9990
473.5	30.00	0.1254	0.9992
473.5	39.86	0.1594	0.9993
473.5	49.86	0.1935	0.9993
573.2	9.96	0.04402	0.9595
573.2	19.89	0.08693	0.9772
573.2	29.84	0.1266	0.9830
573.2	39.96	0.1649	0.9358
573.2	49.74	0.2032	0.9876

Table 6 Methane + n-Octacosane VLE Data

T, K	P, atm	X_M	Y_M
373.3	9.77	0.05661	1.0
373.3	19.90	0.1128	1.0
373.3	30.04	0.1631	1.0
373.3	40.19	0.2039	1.0
373.3	49.97	0.2435	1.0
473.4	9.78	0.04957	1.0
473.4	19.61	0.1000	1.0
473.4	29.88	0.1431	1.0
473.4	40.36	0.1886	1.0
473.4	49.95	0.2241	1.0
573.3	9.48	0.04928	0.9962
573.3	19.74	0.1020	0.9979
573.3	30.21	0.1520	0.9985
573.3	40.17	0.1951	0.9986
573.3	50.11	0.2299	0.9986

Table 7 Carbon Dioxide + n-Eicosane VLE Data

T, K	P, atm	x_{CD}	y_{CD}
323 3	9. 79	0. 1138	1. 0
323 3	19. 89	0. 2166	1. 0
323 3	30. 21	0. 3048	1. 0
323 3	39. 97	0. 3791	1. 0
323 3	49. 48	0. 4460	1. 0
373. 5	10. 04	0. 08421	1. 0
373. 5	19. 83	0. 1568	1. 0
373. 5	30. 02	0. 2279	1. 0
373 5	39. 63	0. 2855	1. 0
373 5	49. 90	0. 3421	1. 0
473 2	9. 85	0. 05929	0. 9979
473. 2	19. 71	0. 1142	0. 9989
473 2	30. 24	0. 1699	0. 9991
473 2	40. 12	0. 2162	0. 9992
473 2	49. 50	0. 2587	0. 9992
573. 4	9. 76	0. 05280	0. 9563
573 4	19. 93	0. 1045	0. 9748
573 4	29. 64	0. 1506	0. 9812
573 4	40. 64	0. 2007	0. 9846
573 4	49. 97	0. 2367	0. 9861

Table 8 Carbon Dioxide + n-Octacosane VLE Data

T, K	P, atm	x_{CD}	y_{CD}
373.4	10.05	0.1016	1.0
373.4	20.14	0.1838	1.0
373.4	30.01	0.2542	1.0
373.4	40.15	0.3240	1.0
373.4	49.90	0.3787	1.0
473.5	9.87	0.06879	1.0
473.5	20.04	0.1353	1.0
473.5	30.18	0.1944	1.0
473.5	39.89	0.2470	1.0
473.5	49.95	0.2928	1.0
572.5	9.81	0.05965	0.9957
572.5	20.06	0.1223	0.9975
572.5	30.08	0.1755	0.9981
572.5	39.92	0.2261	0.9983
572.5	49.91	0.2702	0.9983

Table 9 Ethane + n-Eicosane VLE Data

T, K	P, atm	x_E	y_E
373.8	9.69	0.1591	1.0
373.8	19.91	0.2836	1.0
373.8	29.90	0.3868	1.0
373.8	39.91	0.4632	1.0
473.7	9.83	0.09604	0.9978
473.7	19.86	0.1754	0.9986
473.7	29.99	0.2514	0.9988
473.7	40.18	0.3142	0.9987
572.9	9.83	0.07307	0.9499
572.9	19.64	0.1389	0.9682
572.9	29.90	0.2058	0.9768
572.9	39.85	0.2620	0.9810

Table 10 Ethane + n-Octacosane VLE Data

T, K	P, atm	x_E	y_E
373.3	9.76	0.1804	1.0
373.3	19.90	0.3215	1.0
373.3	28.82	0.4253	1.0
373.3	40.18	0.5039	1.0
473.3	9.82	0.1130	1.0
473.3	19.87	0.2069	1.0
473.3	29.81	0.2873	1.0
473.3	37.46	0.3348	1.0
573.2	9.62	0.08395	0.9957
573.2	19.76	0.1663	0.9973
573.2	29.83	0.2355	0.9976
573.2	39.87	0.2968	0.9977

Table 11 Henry's Constants of Gases in Waxes

	100 C	200 C	300 C
H_2/C_{20}	876 atm	545 atm	388 atm
H_2/C_{28}	679	493	347
CO/C_{20}	523	424	321
CO/C_{28}	435	365	293
CH_4/C_{20}	200	220	207
CH_4/C_{28}	161	187	187
$CO2/C_{20}$	112	159	171
$CO2/C_{28}$	91.8	136	154
C_2H_4/C_{20}	56.8	95.6	123
C_2H_4/C_{28}	47.0	78.3	108

Table 12 Correlation with RKS Equation and Quadratic Mixing Rules

	one parameter		two parameters					
	ka	K1 AAD %	ka	kb	K1 AAD %	ka0	ka1 x10**3	K1 AAD %
H2/C20	0.5418	3.5	0.2370	-0.0125	3.6	0.3576	0.4448	3.3
H2/C28	0.2729	1.9	0.0365	-0.0072	1.6	0.3475	-0.1738	1.8
CO/C20	0.1432	3.1	-0.2889	-0.0376	3.2	0.2477	-0.2391	3.2
CO/C28	0.0211	5.9	0.4241	0.0253	5.1	0.5208	-1.1859	2.1
CH4/C20	-0.0128	2.1	0.0294	0.0070	2.1	0.0043	-0.0298	2.1
CH4/C28	-0.1039	4.7	-0.0381	0.0081	4.8	0.1309	-0.5439	1.5
C2H6/C20	-0.0246	3.7	0.0437	0.0266	1.7	-0.0157	-0.0166	3.6
C2H6/C28	-0.0700	5.8	0.0294	0.0297	3.3	-0.0150	-0.3721	3.8
CO2/C20	0.1029	3.3	0.1474	0.0132	2.4	-0.0046	-0.1661	2.5
CO2/C28	0.0329	5.8	0.1304	0.0197	4.5	0.2177	-0.4808	2.3

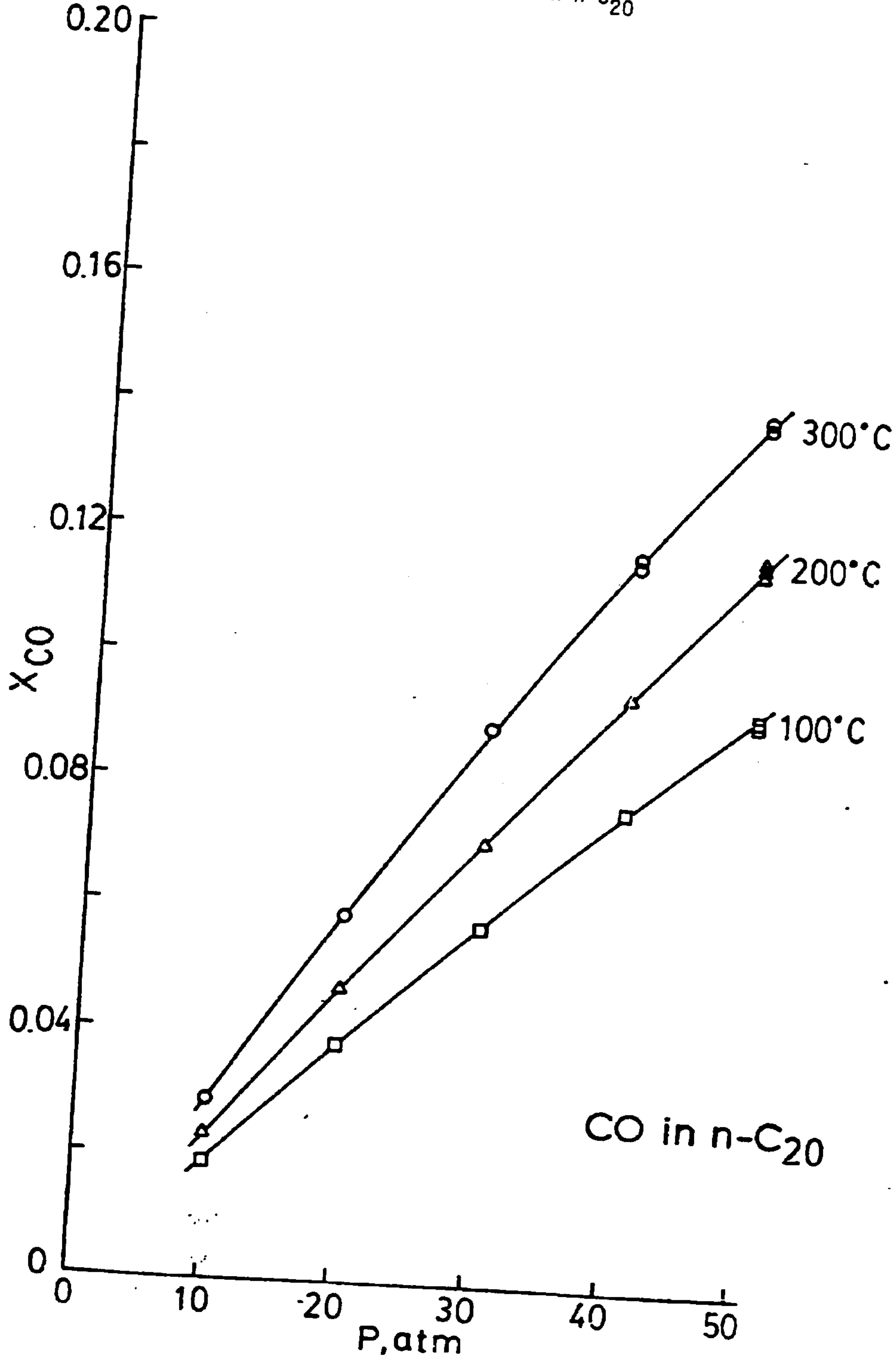
Table 13 Correlation with PR Equation and Quadratic Mixing Rules

	one parameter		two parameters					
	ka	K1 AAD %	ka	kb	K1 AAD %	ka0	ka1 x10**3	K1 AAD %
H2/C20	0.4246	3.4	0.0419	-0.0233	3.0	0.6461	-0.5191	3.1
H2/C28	0.2528	3.3	-0.2975	-0.0244	1.3	0.6263	-0.8654	1.7
CO/C20	0.1282	4.4	-0.4876	-0.0642	3.4	0.3874	-0.6167	2.8
CO/C28	0.0303	7.6	-0.3212	-0.0268	7.4	0.5538	-1.2416	1.8
CH4/C20	-0.0159	2.4	-0.0039	0.0022	2.4	0.0543	-0.1711	1.9
CH4/C28	-0.0986	5.8	-0.0765	0.0030	5.9	0.1507	-0.5879	1.5
C2H6/C20	-0.0300	3.7	0.0384	0.0274	1.3	-0.0138	-0.0413	3.7
C2H6/C28	-0.0753	6.5	0.0232	0.0314	3.1	0.1009	-0.4071	3.7
CO2/C20	0.0821	4.8	0.1379	0.0171	3.8	0.1244	0.0671	2.2
CO2/C28	0.0086	7.1	0.1109	0.0220	6.1	0.1357	-0.0648	1.8

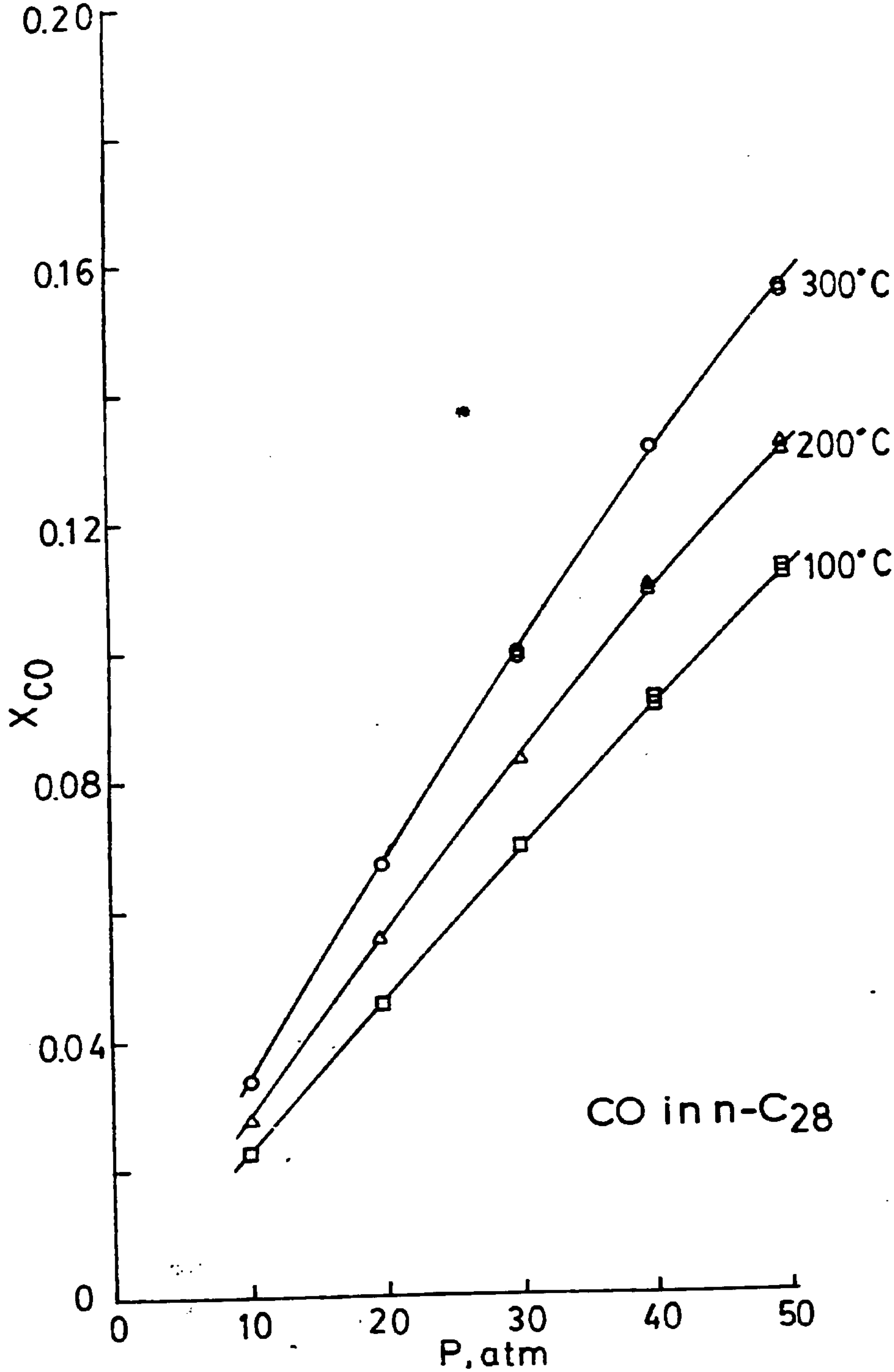
Table 14 Correlation with CCOR Equation and Quadratic Mixing Rules

	two parameters			three parameters			
	ka	kc	K1 AAD %	ka0	ka1 x10**3	kc	K1 AAD %
H2/C20	0.1717	-0.1065	2.2	0.9711	-1.0527	-0.0789	1.7
H2/C28	1.2217	-0.0927	3.9	1.0606	0.2106	-0.0964	3.9
CO/C20	0.3786	-0.0672	1.3	0.1709	0.2679	-0.0769	1.1
CO/C28	1.1709	-0.0604	4.9	-0.0968	1.6242	-0.1007	2.3
CH4/C20	0.3579	-0.0274	4.1	-0.0341	0.6016	-0.0480	1.3
CH4/C28	0.6496	-0.0503	13.2	-0.5074	1.9476	-0.8566	2.6
C2H6/C20	0.0032	0.0230	12.7	-0.4927	1.2087	-0.0183	2.1
C2H6/C28	-0.1225	-0.0219	16.3	-0.8842	2.0390	-0.0681	1.4
CO2/C20	-0.0287	-0.0021	6.7	-0.3629	0.9390	-0.0437	2.9
CO2/C28	0.0504	-0.0146	10.2	-0.7330	2.0257	-0.0802	1.7

Figure . Solubility of CO in n-C_{20}



'gure 2. Solubility of CO in n 28



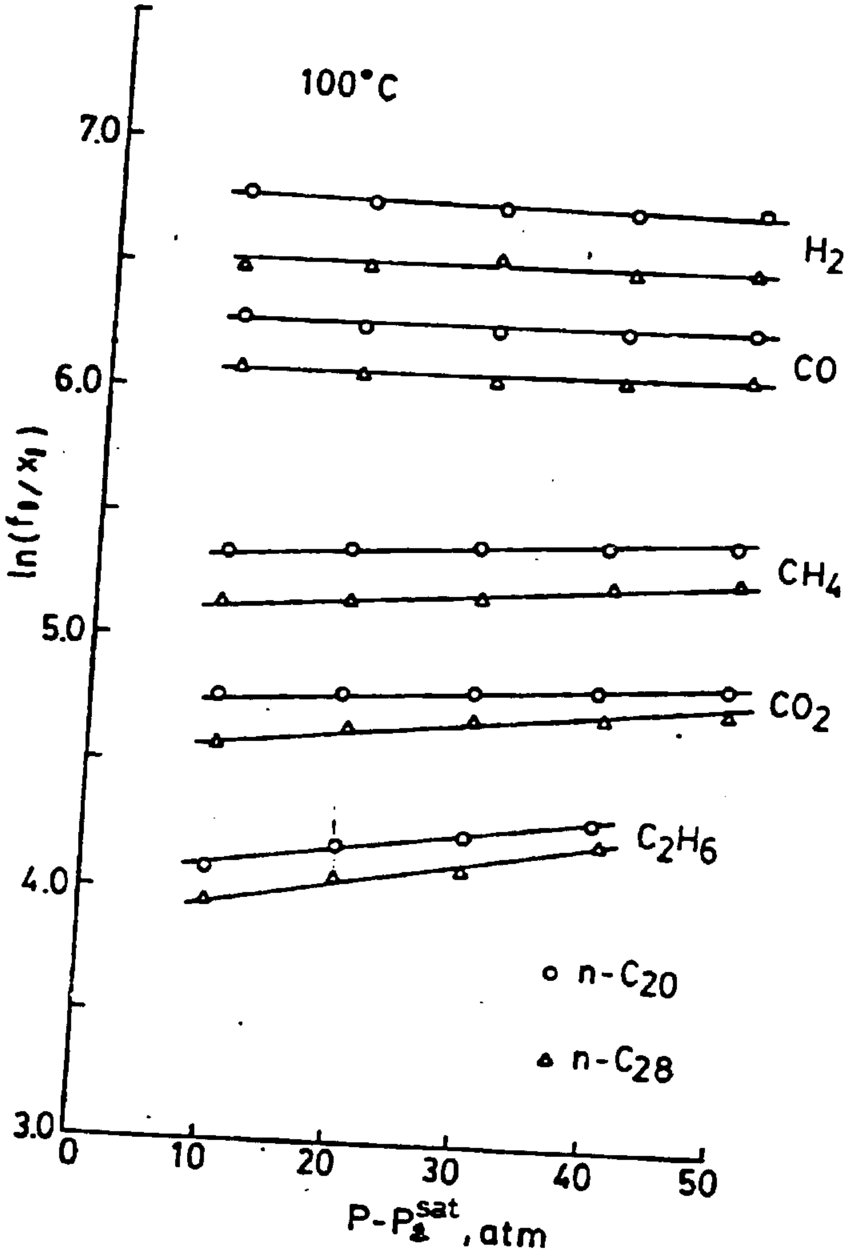


Figure 3. Correlation of data with Krichevsky-Kasarnovsky equation at 100 C.

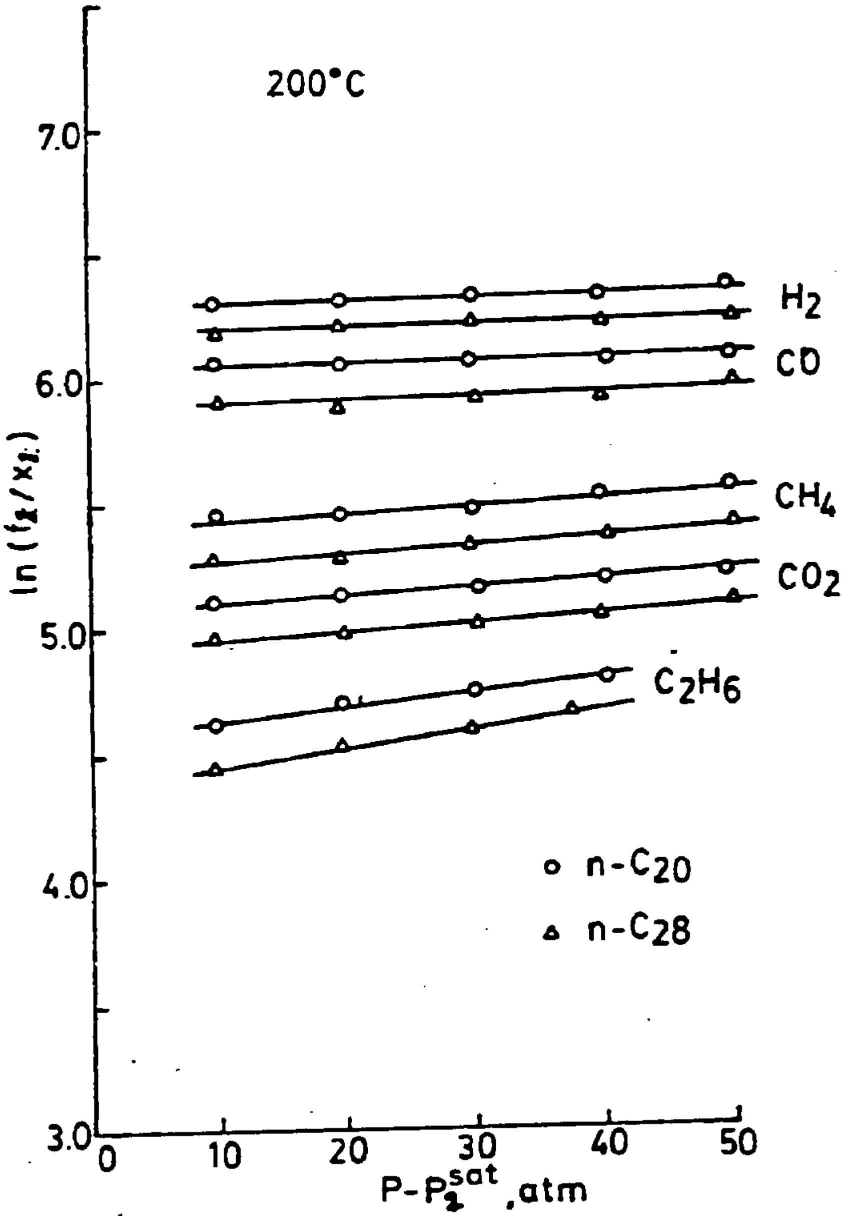


Figure 4. Correlation of data with Krichevsky-Kasarnovsky equation at 200 C.

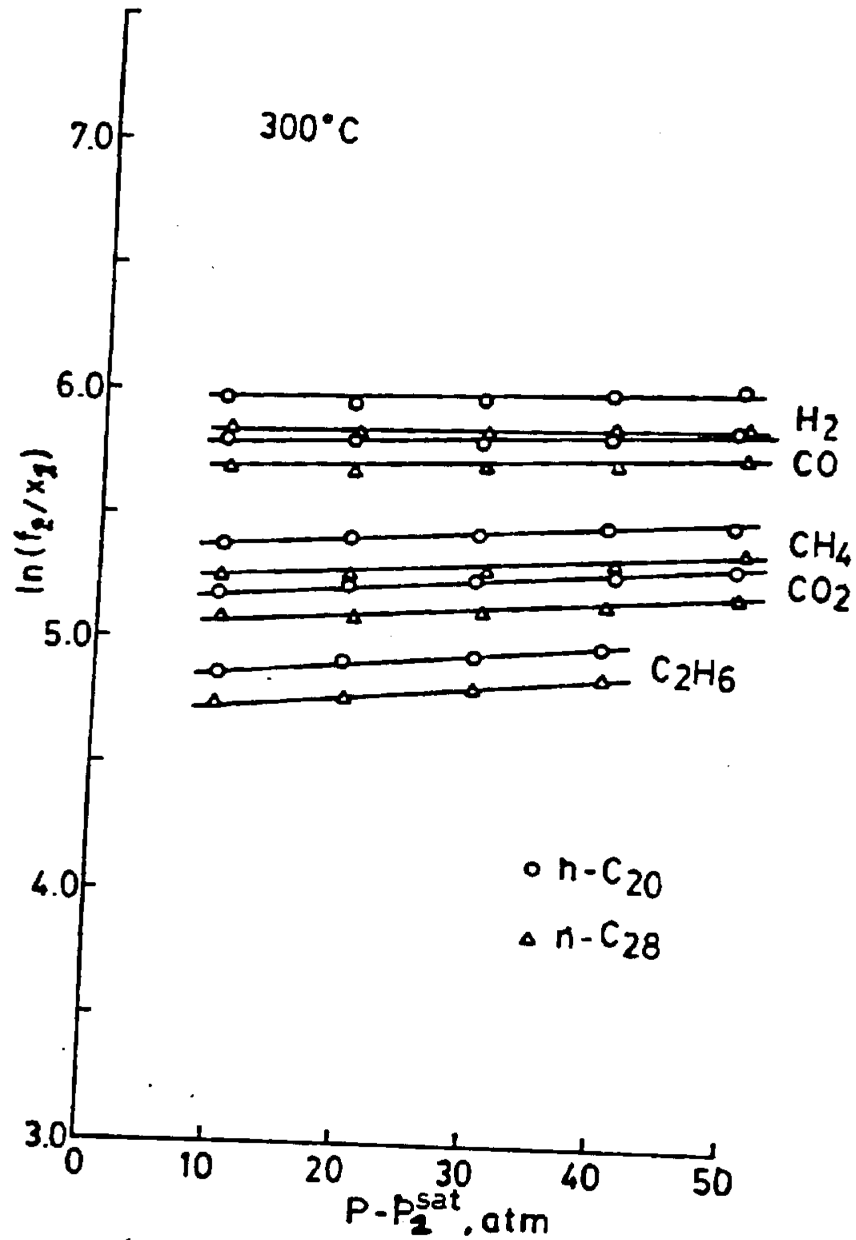


Figure 5. Correlation of data with Krichevsky-Kasarnovsky equation at 300 C.

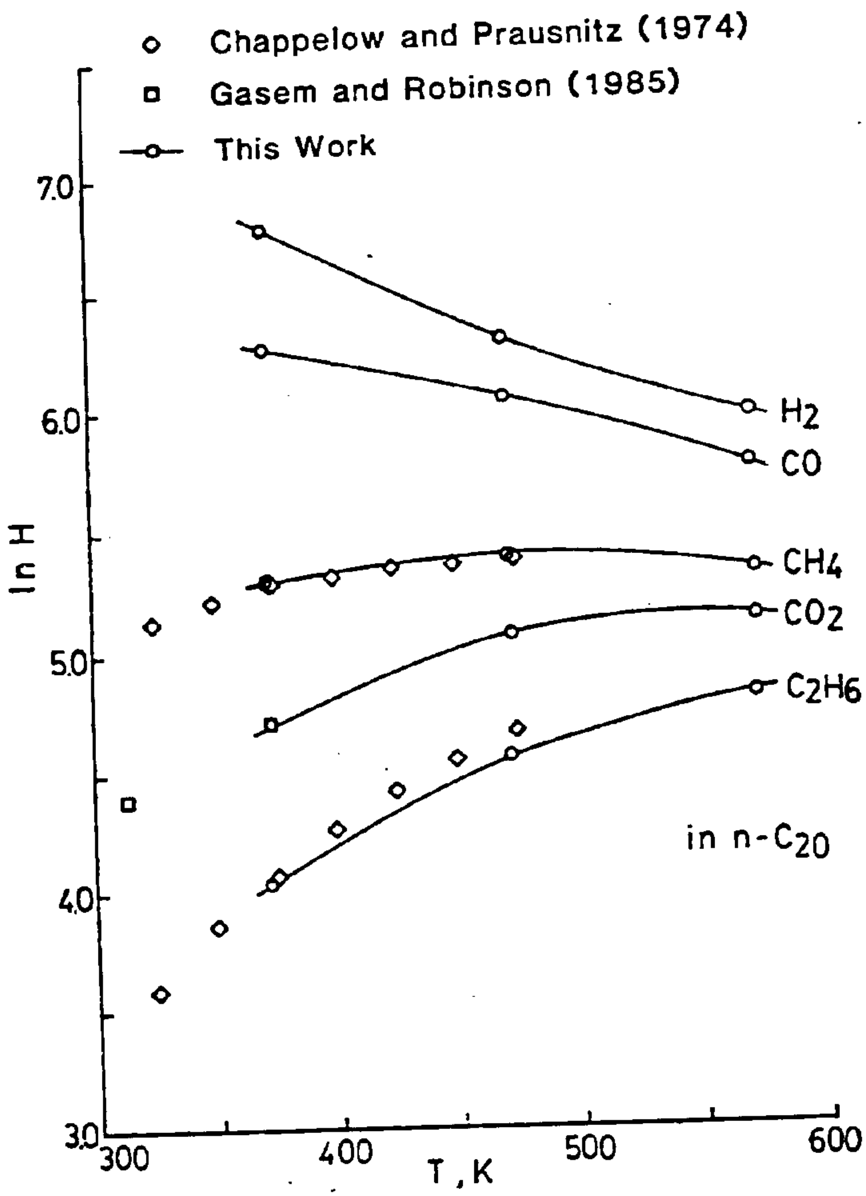


Figure 6. Henry's Constants in n-Eicosane.

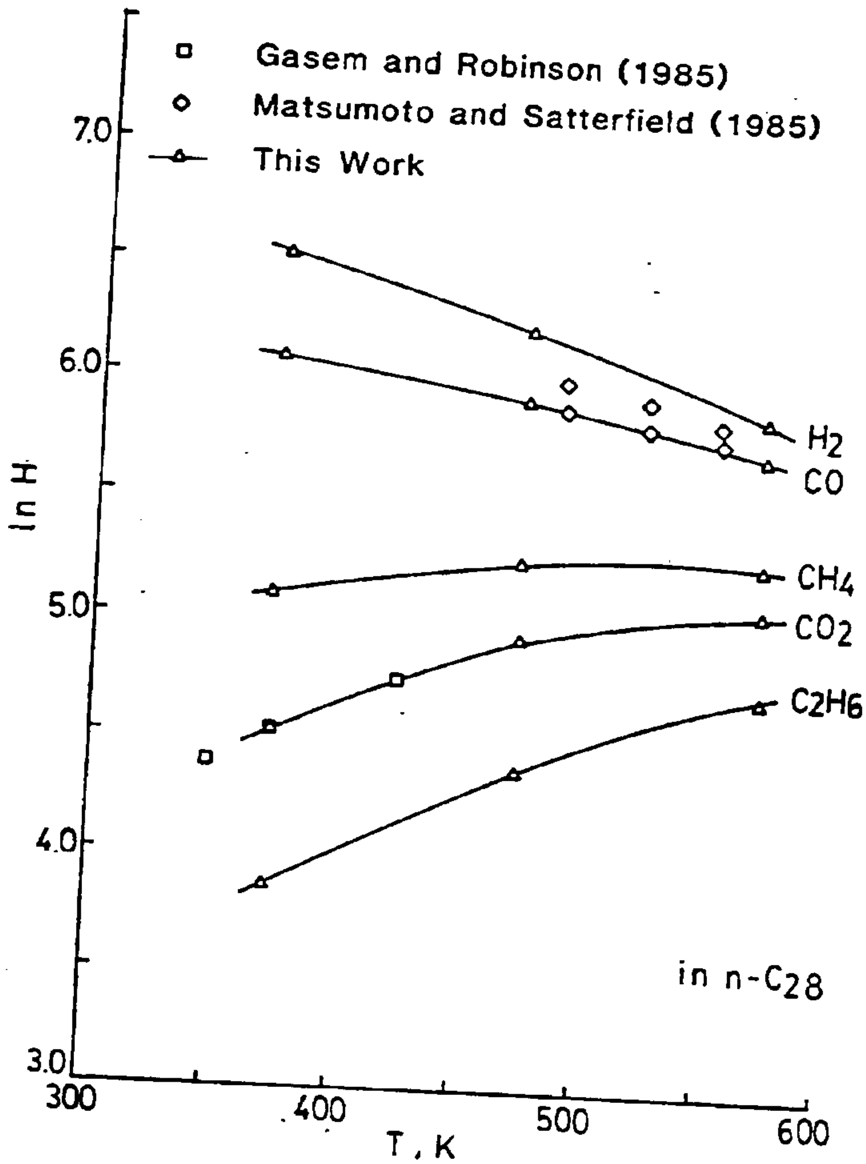


Figure 7. Henry's Constants in n-Octacosane.

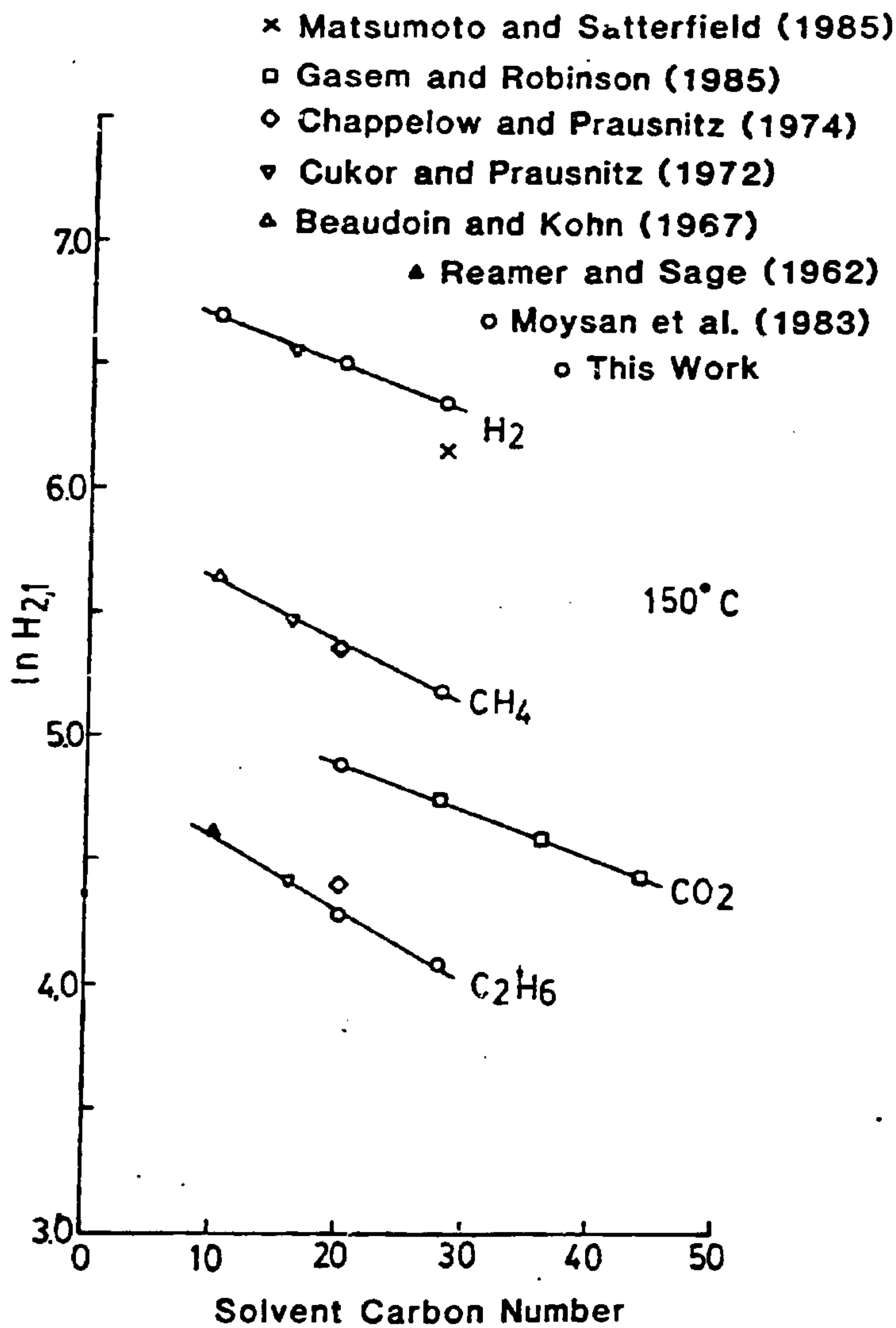


Figure 8. Henry's Constants in n-Paraffins.