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SUMMARY

During the present reporting period, the solubilities of hydrogen in naphthalene, phenanthrene and pyrene were measured at temperatures from 373.2 to 433.2 K (212.0 to 320.0 °F) and pressures to 21.7 MPa (3,147 psia). These data are described with root-mean-square (RMS) errors typically less than 0.001 in mole fraction by the Soave-Redlich-Kwong and Peng-Robinson equations of state when a single interaction parameter, C_{ij}, is used for each isotherm.

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EQUILIBRIUM AND VOLUMETRIC DATA AND MODEL DEVELOPMENT FOR COAL FLUIDS

Report for the Period
January 1, 1993 to March 31, 1993

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EQUILIBRIUM AND VOLUMETRIC DATA AND MODEL DEVELOPMENT FOR COAL FLUIDS

ABSTRACT

The proper design, operation, and optimization of coal conversion and utilization processes depend heavily on knowledge of the phase behavior of the mixtures encountered in these processes. Frequently quoted statistics suggest that in conventional chemical plants 70% of the capital and 90% of the operation expenses are associated with phase separations. Since multiple stages occur in almost all stages of coal conversion processes - from feed preparation through conversion reactions to product separation - the proper description of phase behavior is important in each step of these processes.

The long term goal of our efforts is to develop accurate predictive methods for description of equilibrium phase properties for a variety of types of mixtures and operating conditions. The specific objectives of the work specified herein include:

(1) development of an experimental facility having the capability to provide data on equilibrium phase compositions (solubilities) and liquid densities, and doing so with greater accuracy and speed than our previous facility,

(2) measurement of equilibrium phase properties for systematically selected mixtures - specifically those containing important solute gases (such as hydrogen, carbon dioxide, methane, ethane, carbonyl sulfide, ammonia) in a series of heavy paraffinic, naphthenic and aromatic solvents (e.g., n-decane, n-eicosane, n-octacosane, n-hexatriacontane, cyclohexane, decalin, perhydrophenanthrene, perhydropyrene, benzene, naphthalene, phenanthrene, pyrene),

(3) testing/development of correlation frameworks for representing the phase behavior of fluids of the type encountered in coal conversion processes, and

(4) generalization of parameters in the correlation frameworks to enable accurate predictions for systems of the type studied, permitting predictions to be made for

systems and conditions other than those for which experimental data are available.

During the present reporting period, the solubilities of hydrogen in naphthalene, phenanthrene and pyrene were measured at temperatures from 373.2 to 433.2 K (212.0 to 320.0 °F) and pressures to 21.7 MPa (3,147 psia). These data are described with root-mean-square (RMS) errors typically less than 0.001 in mole fraction by the Soave-Redlich-Kwong and Peng-Robinson equations of state when a single interaction parameter, C_{ij}, is used for each isotherm.

Solubilities of Hydrogen in Naphthalene, Phenanthrene and Pyrene at Temperatures from 373.2 to 433.2 K and Pressures to 21.7 MPa

By

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Abstract

The solubilities of hydrogen in naphthalene, phenanthrene and pyrene were measured using a static equilibrium cell over the temperature range from 373.2 to 433.2 K and pressures to 21.7 MPa. The uncertainty in these new solubility measurements is estimated to be less than 0.001 in mole fraction. The data were analyzed using the Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations of state. In general, the two equations represent the experimental data well when a single interaction parameter is used for each isotherm.

Introduction

Accurate predictions for the phase behavior of fluid mixtures are at the heart of chemical process design and development. Industrial processes such as petroleum refining, hydrocarbon reforming, coal conversion, enhanced oil recovery, and supercritical separation have created great demand for phase equilibrium data for asymmetric mixtures. These mixtures, which involve small gas solute molecules (such as CO_2, hydrogen, methane, ethane, and CO) and heavy hydrocarbon solvents, pose a challenge to the current predictive models and the associated mixing theories.

As a part of our on-going research dealing with the phase behavior of asymmetric mixtures, the solubilities of methane, ethane, CO_2 and CO in systematically-chosen solvents (heavy paraffinic, naphthenic and aromatic hydrocarbons) have been measured and correlated [1-7]. In this study, we report new binary measurements for the solubilities of hydrogen in naphthalene, phenanthrene and pyrene. These data cover temperatures from 373.2 to 433.2 K and pressures to 21.7 MPa. The newly acquired data have been correlated using the SRK [8] and PR [9] equations of state and compared with measurements reported by Malone and Kobayashi [10].

Experimental Method

A variable-volume, static-type blind equilibrium cell was used in this study. For a given binary mixture of known composition, the bubble point pressure is identified graphically from the discontinuity in compressibility of the mixture as it passes from the two-phase state to the single liquid phase. This method consists of introducing known amounts of well degassed pure components into a variable-volume thermostated equilibrium cell. The volume of the equilibrium mixture is varied by the introduction and withdrawal of mercury. Two steel balls are placed in the equilibrium cell and the cell is rocked 45 degrees about the horizontal level to hasten the establishment of equilibrium. Details of the apparatus and experimental procedure are described by Darwish [11]. The measurement uncertainties are estimated to be 0.1 K in temperature and less than 0.001 in mole fraction. The estimated uncertainty in the bubble point pressure, which is dependent on the steepness of the pressure-composition relation, is on the order of 0.06 MPa for the systems studied here. A detailed error analysis is given by Darwish [11].

Materials

The hydrogen used in this study had a stated purity of 99.9995% and was supplied by Union Carbide Corporation. The naphthalene, phenanthrene and pyrene were supplied by the Aldrich Chemical Company and have stated purities of 99+ %, 98+ %, and 99+ %, respectively. No further purification of these chemicals was attempted.

Results and Data Correlation

The hydrogen solubility data are presented in Tables I to III. The effect of temperature and pressure on the solubility of hydrogen in naphthalene is shown in Figure 1. A trend of increasing solubility with increased temperature and pressure is observed within the experimental range considered. As shown in Figure 2, the solubilities of hydrogen in phenanthrene exhibit the same trend as that of hydrogen and naphthalene mixtures. For hydrogen and pyrene mixtures, the solubilities are measured only for one isotherm, 433.2 K. These are shown in Figure 3.

A comparison of our binary data for the solubility of hydrogen in phenanthrene with those of Malone and Kobayashi [10] is given in Figure 4. The comparison is shown in terms of solubility deviations generated by comparing optimum SRK predictions to the experimental measurements. For this purpose, the interaction parameter, C_{ij}, of the SRK equation of state (discussed below) was regressed from our data at 423.2 K. Figure 4 indicates good agreement between our data and those of Malone and Kobayashi.

The SRK [8] and PR [9] cubic equations of state were used to correlate the experimental data. The SRK equation is given below; similar relations are given elsewhere for the Peng-Robinson equation [9].

$$p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \tag{1}$$

where

$$a(T) = a_c \alpha(T) \tag{2}$$

$$b = 0.08664 RT_c / p_c \tag{3}$$

and

$$a_c = 0.42748 R^2 T_c^2 / p_c \tag{4}$$

$$a(T)^{1/2} = 1 + k(1 - T_r^{1/2}) \tag{5}$$

$$k = 0.480 + 1.574\omega - 0.176\omega^2 \tag{6}$$

To apply the SRK or PR equations of state to mixtures, the values of a and b can be determined using the mixing rules [4]

$$a = \sum_i^N \sum_j^N z_i z_j (1 - C_{ij})(a_i a_j)^{1/2} \tag{7}$$

$$b = 0.5 \sum_i^N \sum_j^N z_i z_j (1 + D_{ij})(b_i + b_j) \tag{8}$$

In Equations 7 and 8, the summations are over all chemical species and C_{ij} and D_{ij} are empirical interaction parameters characterizing the binary interactions between components "i" and "j". Values of these parameters were determined by fitting the experimental data to minimize the objective function, SS, which represents the sum of square errors in predicted bubble point pressures. In this study, the interaction parameter D_{ij} was set zero.

$$SS = \sum_{i}^{n} (P_{exp} - P_{calc})_i^2 \tag{9}$$

Further details on the data reduction techniques are given by Gasem [12]. The input parameters for the pure components (acentric factors, critical temperatures and critical pressures) required by the SRK and PR equations of state, together with the literature sources, are presented in Table IV.

The equation-of-state representations of the solubilities for the systems considered are shown in Tables V to VII. In general, the SRK and PR equations are capable of describing the data with RMS errors usually less than 0.001 in mole fraction when a single interaction parameter, C_{ij}, is used per isotherm. Our data reduction indicates that the interaction parameter, C_{ij}, is highly dependent on temperature. Moreover, the SRK and PR equations of state, in general, exhibit comparable abilities in representing the data using a single interaction parameter. Data regressions which included a second interaction parameter, D_{ij}, were not attempted in this study.

Henry's Constants

By definition, Henry's constant of hydrogen (1) in a hydrocarbon solvent (2) is given as:

$$H_{1,2} = \underset{\lim x_1 \to 0}{(f_1 / x_1)} = \underset{\lim x_1 \to 0}{(\varphi_1 p)} \tag{10}$$

Estimates for Henry's constant were obtained for the present data using SRK and PR equations of state in accordance with the above definition. Values for the Henry's constants, along with the interaction parameters associated with them, are given in Tables V to VII. In general, the SRK EOS produces slightly lower $H_{1,2}$ values (~ 1% lower) than those obtained form the PR EOS.

Conclusions

Data have been obtained for the solubilities of hydrogen in naphthalene, phenanthrene and pyrene at temperatures from 373.2 to 433.2 K and pressures up to 21.7 MPa. These data are well described by the SRK and PR equations of state. Interaction parameters for these equations along with estimates for Henry's constants have been obtained for the binary systems considered.

List of Symbols

$a(T)$	energy parameter in the SRK or PR EOS
C_{ij}, D_{ij}	binary interaction parameters in the SRK or PR EOS
$H_{1,2}$	Henry's constant
f_1	fugacity of component 1
N	number of components in mixture
n	number of data points
p	pressure
R	gas constant
SS	objective function (defined by Eq. 9)
T	temperature
v	molar volume
x	liquid mole fraction of hydrogen (solubility)
Z	compressibility factor
z_i	mole fraction of component "i" in a mixture

Greek letters

α	temperature dependent parameter in Eq. 2
φ_1	fugacity coefficient of component 1
ω	acentric factor

Subscripts

c	critical state
calc	calculated
exp	experimental
i	component "i" in a mixture
r	reduced property

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Acknowledgment

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Table I

Solubility of Hydrogen (1) in Naphthalene (2)

x_1	p/MPa	x_1	p/MPa
---------------------------- 373.2 K (100.0 °C, 212.0 °F) --			
0.0157	5.29	0.0362	12.35
0.0165	5.50	0.0530	18.53
0.0346	11.80	0.0553	19.39
---------------------------- 423.2 K (150.0 °C, 302.0 °F) --			
0.0166	4.29	0.0385	9.95
0.0189	4.84	0.0470	12.46
0.0273	7.06	0.0534	14.08
0.0337	8.77	0.0567	15.21

Table II

Solubility of Hydrogen (1) in Phenanthrene (2)

x_1	p/MPa	x_1	p/MPa
---------------------------- 383.2 K (110.0 °C, 230.0 °F) ----------------------------			
0.0165	6.33	0.0398	15.78
0.0228	8.85	0.0492	19.79
0.0328	12.83	0.0535	21.69
---------------------------- 423.2 K (150.0 °C, 302.0 °F) ----------------------------			
0.0187	5.89	0.0391	12.53
0.0226	7.14	0.0514	16.74
0.0354	11.31	0.0557	18.35

Table III

Solubility of Hydrogen (1) in Pyrene (2)

x_1	p/MPa	x_1	p/MPa
---------------------------- 433.2 K (160.0 °C, 320.0 °F) ----------------------------			
0.0158	5.17	0.0358	11.91
0.0185	6.05	0.0498	16.97
0.0325	10.80	0.0575	19.73

Table IV

Critical Pressure, p_c, Critical Temperature, T_c, and Acentric Factor, ω, Used in the SRK and PR Equations of State

Component	p_c/MPa	T_c/K	ω	Reference
Hydrogen	1.30	33.2	-0.218	13
Naphthalene	4.05	748.4	0.302	14
Phenanthrene	3.30	873.2	0.540	15
Pyrene	2.60	938.2	0.830*	16

* Turek, E. A., AMOCO Production Company, Tulsa, OK, Personal Communication (1988)

Table V

SRK and PR Equation of State Representations of the Solubility of Hydrogen (1) in Naphthalene (2)

T/K	SRK Parameters (PR Parameters) C_{12}	Error in Hydrogen Fraction		SRK Henry's Constant (PR Henry's Constant) bar
		RMS	|MAX|	
373.2	0.3685	0.0006	0.0009	3065.0
	(0.3895)	(0.0006)	(0.0008)	(3079.0)
423.2	0.4278	0.0005	0.0007	2383.1
	(0.4127)	(0.0004)	(0.0006)	(2401.7)
373.2 and 423.2	0.3865	0.0011	0.0016	
	(0.3971)	(0.0007)	(0.0010)	

Table VI

SRK and PR Equation of State Representations of the Solubility of Hydrogen (1) in Phenanthrene (2)

T/K	SRK Parameters (PR Parameters) C_{12}	Error in Hydrogen Fraction RMS	|MAX|	SRK Henry's Constant (PR Henry's Constant) bar
383.2	0.3245	0.0005	0.0007	3536.1
	(0.3766)	(0.0005)	(0.0007)	(3542.9)
423.2	0.3665	0.0005	0.0007	2913.3
	(0.3940)	(0.0004)	(0.0006)	(2928.5)
383.2 and 423.2	0.3376	0.0008	0.0012	
	(0.3824)	(0.0006)	(0.0009)	

Table VII

SRK and PR Equation of State Representations of the Solubility of Hydrogen (1) in Pyrene (2)

T/K	SRK Parameters (PR Parameters) C_{12}	Error in Hydrogen Fraction RMS	|MAX|	SRK Henry's Constant (PR Henry's Constant) bar
433.2	0.4309	0.0005	0.0007	3053.3
	(0.4620)	(0.0005)	(0.0006)	(3061.5)

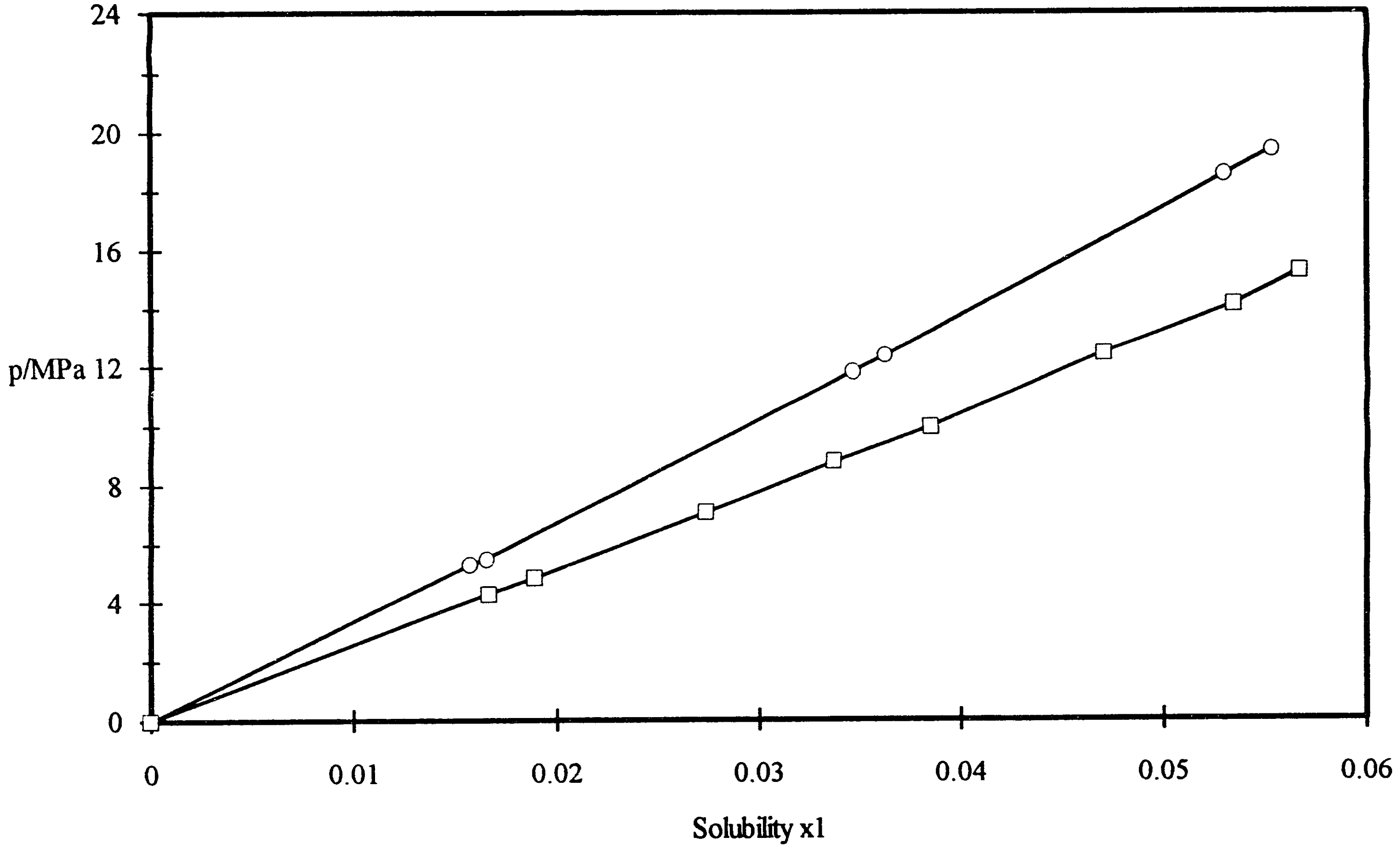

Figure 1. Solubility of Hydrogen in Naphthalene. ○ 373.2 K; ☐ 423.2 K

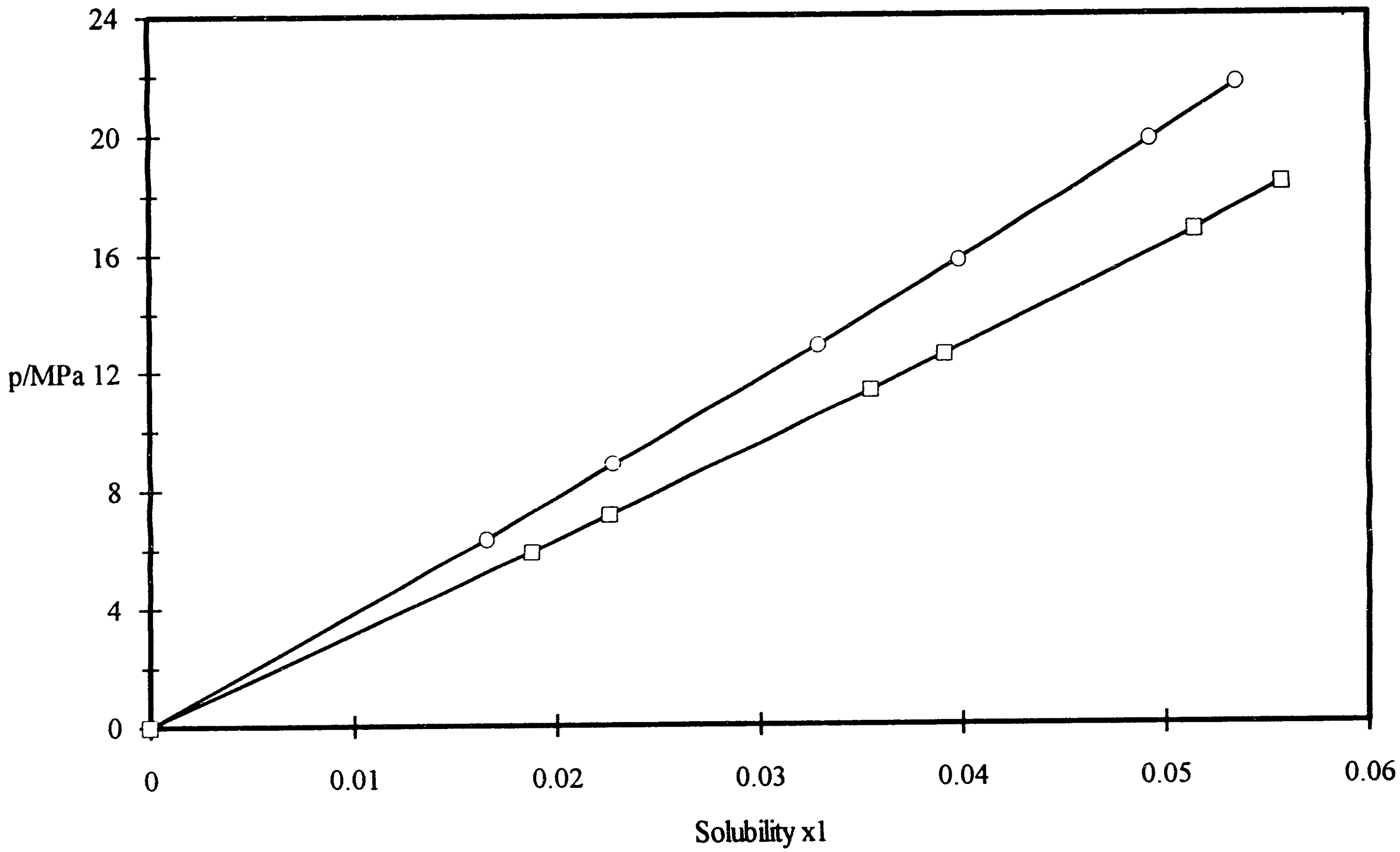

Figure 2. Solubility of Hydrogen in Phenanthrene. ○ 383.2 K; ☐ 423.2 K

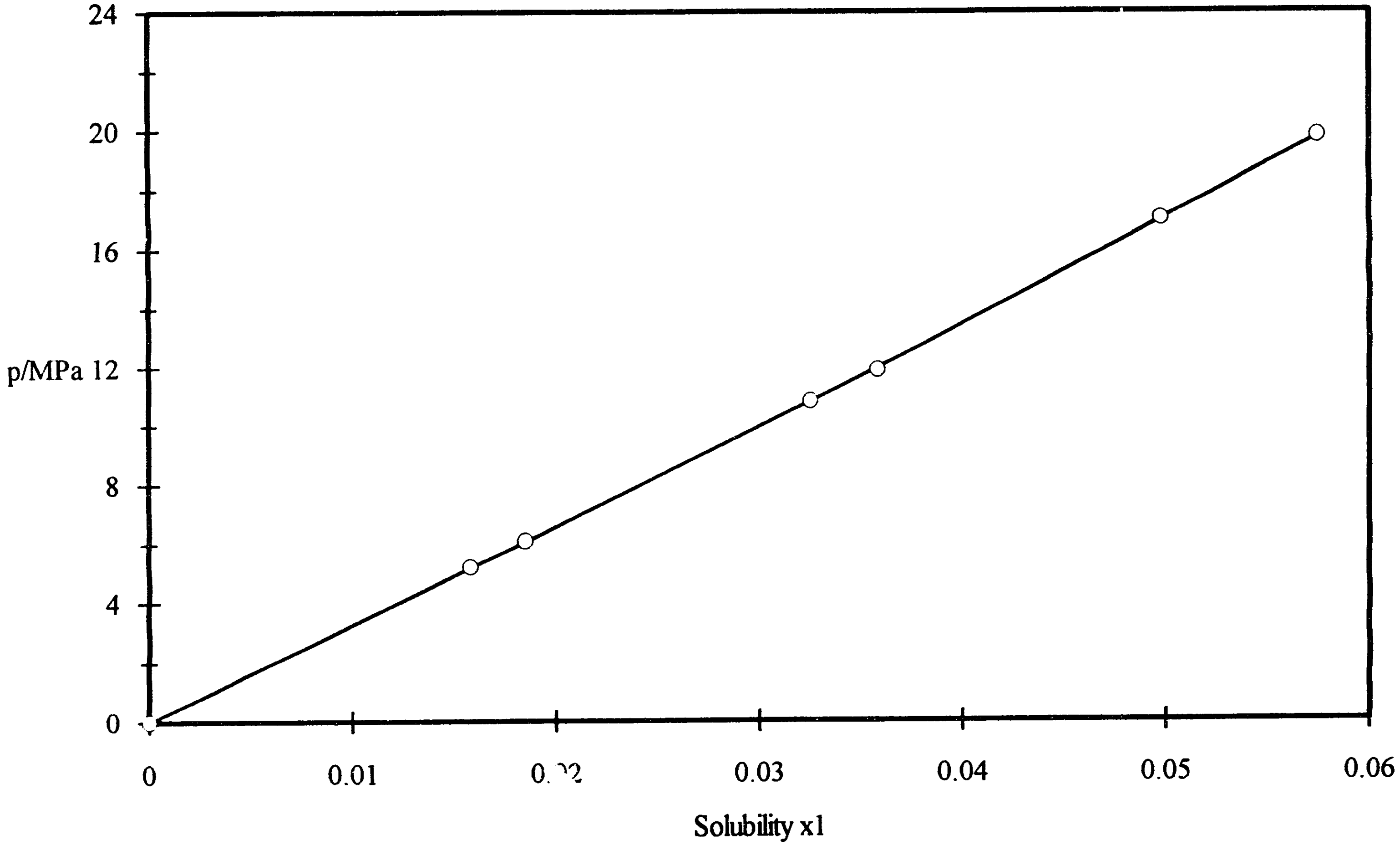

Figure 3. Solubility of Hydrogen in Pyrene at 433.2 K.

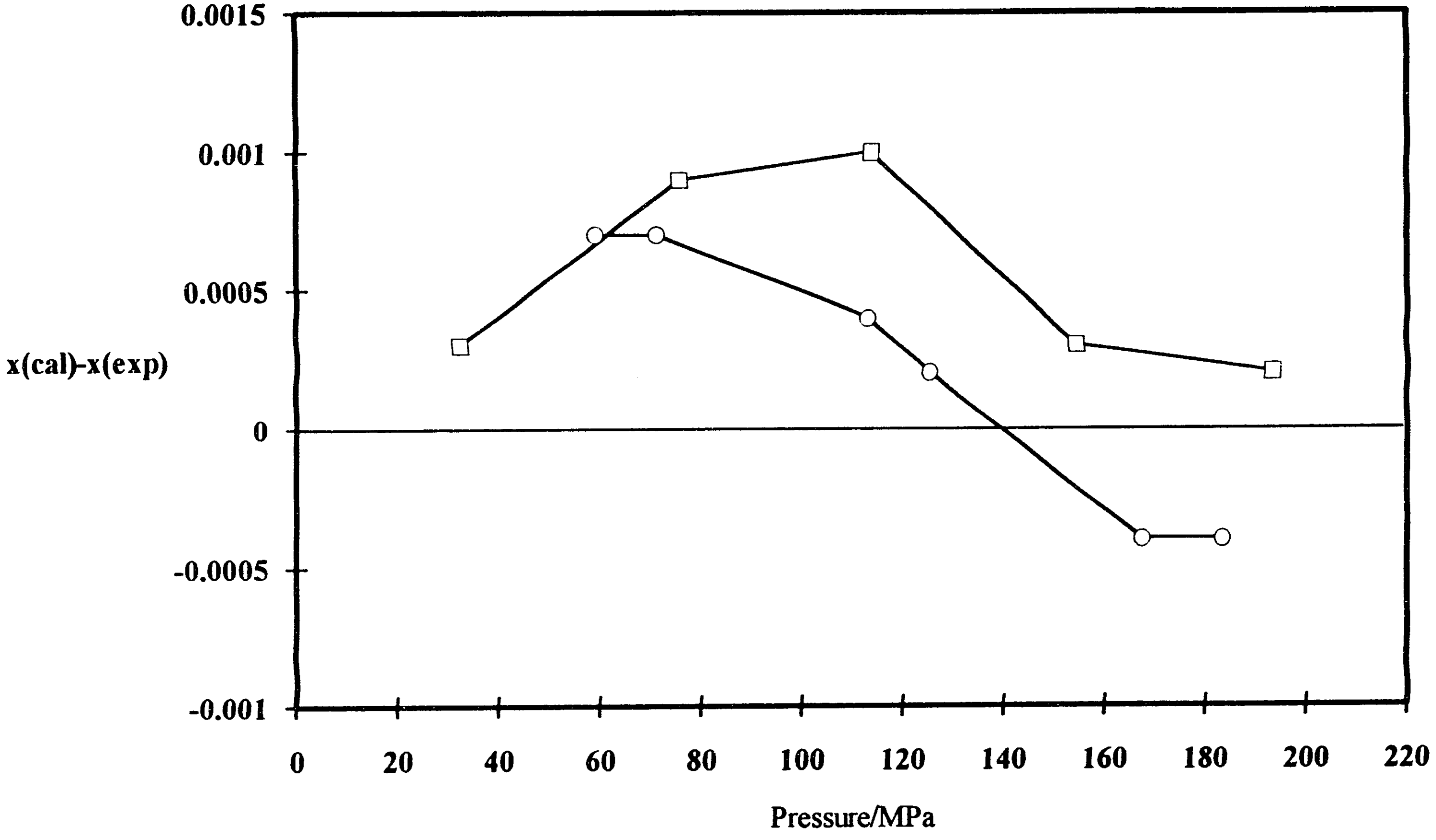

Figure 4. Deviation Plot of Hydrogen Solubilities in Phenanthrene at 423.2 K.

○ This work; □ Malone and Kobayashi [10]

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