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PROJECT TITLE: "Equilibrium and Volumetric Data and Model Development for Coal
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SUMMARY

During the present reporting period, the solubilities of nitrogen in n-decane and in n-eicosane were measured at temperatures from 323.2 to 423.2 K (122.0 to 302.0 °F) and pressures to 17.2 MPa (2,499 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
April 15, 1993 to July 15, 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 phases 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 the description of equilibrium phase properties for a variety of types of mixtures and operating conditions. The specific objectives of the present work 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 nitrogen, 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) development and testing 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 nitrogen in n-decane and in n-eicoane⁵ were measured at temperatures from 323.2 to 423.2 K (122.0 to 302.0 °F) and pressures to 17.2 MPa (2,499 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 Nitrogen in n-Decane, n-Eicosane
at Temperatures from 323.2 to 423.2 K and
Pressures to 17.2 MPa**

By

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Abstract

The solubilities of nitrogen in n-decane and in n-eicosane were measured using a static equilibrium cell at temperatures from 323.2 to 423.2 K and pressures to 17.2 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

As a part of our on-going research dealing with the phase behavior of asymmetric mixtures, the solubilities of methane, ethane, CO₂ and CO in systematically-chosen solvents (heavy paraffinic, naphthenic and aromatic hydrocarbons) have been measured and correlated [1-7]. In the present study, we report new binary measurements for the solubilities of nitrogen in n-decane and in n-eicosane. These data cover temperatures from 323.2 to 423.2 K and pressures to 17.2 MPa. The newly acquired data have been correlated using the SRK [8] and PR [9] equations of state and compared with measurements reported by Azarnoosh and McKetta [10] and Llave and Chung [13].

Currently, few data are available for mixtures involving nitrogen and heavy hydrocarbons. For example, hexadecane is the heaviest member of the normal paraffin homologous series for which nitrogen vapor-liquid equilibrium data exist [17]. Therefore, the present data constitute a valuable addition to the literature.

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]. Experimental 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 for these type of measurements is given by Darwish [11].

Materials

The nitrogen used in this study had a stated purity of 99.9995% and was supplied by Liquid Air, Inc. The n-decane and n-eicosane were supplied by the Aldrich Chemical Company and have stated purities of 99+ %. No further purification of these chemicals was attempted.

Results and Data Correlation

The nitrogen solubility data are presented in Tables I to II. The effect of temperature and pressure on the solubility of nitrogen in n-decane 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 nitrogen in n-eicosane exhibit the same trend as that of nitrogen in n-decane.

Comparisons of our data for nitrogen in n-decane with those of Azarnoosh and McKetta [10] and Llave and Chung [13] are given in Figures 3-5. These comparisons are shown in terms of solubility deviations generated by comparing optimum SRK predictions to the experimental measurements. For this purpose, the interaction parameters, C_{ij} , of the SRK equation of state (discussed below) were regressed from our data at 344.3, 377.6, and 423.2 K. Figures 3-5 indicate disagreement between our data and those of Azarnoosh and McKetta [10] and Llave and Chung [13].

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].

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

where

$$a(T) = a_c \alpha(T) \quad (2)$$

$$b = 0.08664RT_c / p_c \quad (3)$$

and

$$a_c = 0.42748R^2T_c^2 / p_c \quad (4)$$

$$\alpha(T) = [1 + k(1 - T_r^{1/2})]^2 \quad (5)$$

$$k = 0.480 + 1.574\omega - 0.176\omega^2 \quad (6)$$

The values of a and b were determined using the following mixing rules [4].

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

$$b = \sum_i^N z_i b_i \quad (8)$$

In Equations 7 and 8, the summations are over all chemical species and C_{ij} is an empirical interaction parameter characterizing the binary interactions between components "i" and "j". Values of C_{ij} 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, where

$$SS = \sum_i^n (P_{exp} - P_{calc})_i^2 \quad (9)$$

Further details on the data reduction technique is 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 III.

The equation-of-state representation of the solubilities for the systems considered are shown in Tables IV to V. 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 parameters, C_{ij} , are temperature dependent and larger in magnitude than typically obtained for other solutes [1-7], especially for the nitrogen + n-eicosane system. Moreover, the SRK and PR equations of state, in general, exhibit comparable abilities in representing the data using a single interaction parameter.

Henry's Constants

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

$$H_{1,2} = \lim_{x_1 \rightarrow 0} (f_1 / x_1) = (\phi_1 p) \lim_{x_1 \rightarrow 0} \quad (10)$$

Estimates for Henry's constant were obtained for the present data using the 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 IV to V. In general, the SRK EOS produces slightly lower $H_{1,2}$ values (~ 1% lower) than those obtained from the PR EOS.

Conclusions

Data have been obtained for the solubilities of nitrogen in n-decane and in n-eicosane at temperatures from 323.2 to 423.2 K and pressures up to 17.2 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}	binary interaction parameter 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 nitrogen (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
cal	calculated
exp	experimental
i	component "i" in a mixture
r	reduced property

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4. Deviation Plot of Nitrogen Solubilities in n-Decane at 377.6 K. $\circ$ This Work; Δ Azarnoosh and McKetta [10]
5. Deviation Plot of Nitrogen Solubilities in n-Decane at 410.9 K. $\circ$ This Work; Δ Azarnoosh and McKetta [10]

Table I
Solubility of Nitrogen (1) in n-Decane (2)

x_1	P/MPa	x_1	P/MPa
----- 344.3 K (71.1 °C, 160.0 °F) -----			
0.0556	4.33	0.1178	9.84
0.0590	4.61	0.1202	10.06
0.0633	4.97	0.1539	13.40
0.1087	8.99	0.1578	13.81
----- 377.6 K (104.4 °C, 220.0 °F) -----			
0.0568	4.05	0.1662	13.15
0.0689	4.97	0.1708	13.63
0.1158	8.73	0.1967	16.04
0.1271	9.66		
----- 410.9 K (137.8 °C, 280.0 °F) -----			
0.0598	3.91	0.1343	9.25
0.0749	4.92	0.1690	11.99
0.1162	7.89	0.1894	13.61

Table II
Solubility of Nitrogen (1) in n-Eicosane (2)

x_1	P/MPa	x_1	P/MPa
----- 323.2 K (50.0 °C, 122.0 °F) -----			
0.0610	4.49	0.1292	10.61
0.0689	5.13	0.1413	11.90
0.0704	5.25	0.1789	16.22
0.0967	7.54	0.1866	17.23
----- 373.2 K (100.0 °C, 212.0 °F) -----			
0.0629	4.03	0.1364	9.74
0.0715	4.61	0.1639	12.10
0.1199	8.33	0.1905	14.61
----- 423.2 K (150.0 °C, 302.0 °F) -----			
0.0679	3.83	0.1445	8.89
0.0930	5.38	0.1728	11.09
0.1278	7.76	0.2121	14.24

Table III
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
Nitrogen	3.390	126.3	0.0390	14
n-Decane	2.096	617.6	0.4885	15
n-Eicosane	1.069	766.6	0.8791	16

Table IV
SRK and PR Equation-of-State Representations
of the Solubility of Nitrogen (1) in n-Decane (2)

T/K	EOS Parameters (SRK/PR) C_{12}	Error in Nitrogen Mole Fraction RMS MAX		EOS Henry's Contant (SRK /PR) bar
344.3	0.2163	0.0006	0.0008	718
	(0.2087)	(0.0005)	(0.0006)	721
377.6	0.2118	0.0010	0.0015	655
	(0.1991)	(0.0007)	(0.0010)	663
410.9	0.2164	0.0013	0.0016	593
	(0.1936)	(0.0008)	(0.0011)	602
344.3, 377.6, 410.9	0.2146	0.0011	0.0022	
	(0.2026)	(0.0013)	(0.0032)	

Table V
SRK and PR Equation-of-State Representations
of the Solubility of Nitrogen (1) in n-Eicosane (2)

T/K	EOS Parameters (SRK/PR) C_{12}	Error in Nitrogen Mole Fraction		EOS Henry's Contant (SRK /PR) bar
		RMS	MAX	
323.2	0.3307	0.0002	0.0003	668
	(0.3211)	(0.0002)	(0.0003)	669
373.2	0.3153	0.0005	0.0010	591
	(0.2956)	(0.0004)	(0.0007)	597
423.2	0.3038	0.0006	0.0010	519
	(0.2707)	(0.0004)	(0.0006)	528
323.2, 373.2, 423.2	0.3248	0.0018	0.0047	
	(0.3096)	(0.0038)	(0.0085)

Figure 1. Solubility of Nitrogen in n-Decane

Figure 2. Solubility of Nitrogen in n-Eicosane

Figure 3. Deviation Plot of Nitrogen Solubilities in n-Decane at 344.3 K;

○ This work; Δ Azarnoosh and McKetta, □ Llave and Chung

Figure 4. Deviation Plot of Nitrogen Solubilities in n-Decane at 377.6 K;

○ This work; Δ Azarnoosh and McKetta

Figure 5. Deviation Plot of Nitrogen Solubilities in n-Decane at 410.9 K;

○ This work; Δ Azarnoosh and McKetta

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