p = number of state variables requiring integral feedback
Q = transformation matrix as defined in Eq. 8
T = matrix used to augment original system as defined in Eq. 16
q = dimension of disturbance vector
r = dimension of control vector
s = Laplace operator
u = control vector, $r \times 1$
V = closed-loop system reciprocal (or left) eigenvector matrix ($V = W^{-1}$)
W = closed-loop system eigenvector matrix
x = state vector, $n \times 1$
x^{ξ} = closed-loop response to disturbance ξ
y = output vector, $m \times 1$
y^{ξ} = output response of the closed-loop system to disturbance ξ

Greek Letters

ϕ = state coefficient matrix for the discrete system
Δ = control coefficient matrix for the discrete system
θ = disturbance coefficient matrix for the discrete system
Λ = $n \times n$ diagonal matrix whose diagonal elements are the eigenvalues of H
ξ = disturbance vector, $q \times 1$

Superscripts

FF = feedforward
-1 = matrix inverse
T = transpose of a vector or matrix
$*$ = pseudoinverse of a matrix
$\sim$ = transformed matrix

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Correlation of Solubility of Hydrogen in Hydrocarbon Solvents

A correlation is developed for the solubility of hydrogen in hydrocarbon solvents at temperatures from 310 to 700 K and pressures to 30 MPa (300 bar). The fugacity of dissolved hydrogen at zero pressure is correlated as a function of solubility parameter and temperature. The high-pressure fugacity is obtained upon applying a Poynting factor for which the required partial molal volume of hydrogen is also correlated in terms of solubility parameter and temperature. The Henry constant of hydrogen is included in the correlation. The correlated results are compared with experimental data for 22 systems of binary and ternary solutions and five narrow-boiling cuts of coal liquids. The overall average absolute deviation for all systems studied is approximately 6%.

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SCOPE

Recent intensified development of hydrofining processes, particularly coal liquefaction, has increased the need for knowledge of hydrogen solubility in heavy hydrocarbons at elevated temperatures and pressures. This information is required for engineering design and analysis of reaction kinetics of hydrofining processes.

Hildebrand and Scott (1950) showed that gas solubility can be correlated with solubility parameter at room temperatures and low pressures. Chao and Seader (1961) and Grayson and Streed (1963) presented correlations for *K*-values of hydrogen with hydrocarbons, in which the regular solution-theory was

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applied to high-pressure systems. Neither of these methods are found to represent the equilibrium ratios for hydrogen well at elevated temperatures.

The objective of this work is to develop a correlation for hydrogen solubility for a wide range of conditions, making use of the large amount of data that has recently become available for solvents of diverse nature, including paraffins, polynuclear aromatics, naphthenes and hetero-atom containing aromatics. The correlation is developed over the temperature range 310 to 700 K and at pressures to 30 MPa (300 bar).

CONCLUSIONS AND SIGNIFICANCE

Hildebrand's solubility parameter is the single most important parameter for the characterization of the power of a solvent for dissolving gases. The usefulness of the solubility parameter exceeds that of the regular-solution equation. A correlation of solubility of hydrogen in diverse solvents has been developed on this basis. At a given temperature, the fugacity of dissolved hydrogen at zero pressure is expressed as a function of solubility parameter only. Fugacity at high pressures is obtained by applying a Poynting factor for which the required partial molal volume of hydrogen is also correlated as a function of solubility parameter and temperature.

Comparison of the correlation with experimental solubility data for 22 systems of binary and ternary mixtures indicates that the average absolute deviation is 6%. When compared to hydrogen solubility in five narrow-boiling cuts of coal liquids, the average deviation is also about 6%.

This new correlation method is useful for engineering and design calculations due to its simplicity and reasonable accuracy. The same method can be applied to other gases. The correlated partial molal volumes of hydrogen are compared with literature data reported by Connolly (1963) and with the correlation of Brelvi and O'Connell (1972). Good agreement is obtained at low temperatures. Significant discrepancy can exist at high temperatures depending on the pressure, because the pressure dependence of partial molal volume is neglected in this correlation.

INTRODUCTION

The solubility of hydrogen in hydrocarbon solvents is of interest in hydrofining of oil and coal where it is basic to engineering design of the processes and to analysis of reaction kinetics. Recent intensified development of coal liquefaction has amplified this interest. As a result, a large amount of new gas-liquid equilibrium data on hydrogen-containing mixtures has been accumulated (Table 5). The new investigations have extended the solvent types to polynuclear aromatics, naphthenes, and N, S, and O-containing aromatics in addition to the usual paraffins. The new investigations have also extended the upper temperature limit to 730 K which is substantially above those of previous investigations.

A number of correlations have been developed for the solubility of hydrogen in hydrocarbon solvents. Most of these are limited to low pressures and room temperatures. Chao and Seader (1961) developed a correlation of vaporization-condensation equilibria of hydrocarbon mixtures to apply at more general conditions. They included the solubility of hydrogen in the correlation. The data base for the hydrogen correlation was limited mainly to paraffin solvents with benzene, toluene, m-xylene, and ethylbenzene the only aromatic solvents, and cyclohexane and methylcyclohexane the only naphthenic solvents. The temperature range of the data base was also quite limited. As a result, the correlation was specifically restricted to temperatures not to exceed 530 K.

Grayson and Streed (1963) modified the correlation of Chao and Seader on the basis of proprietary data on hydrogen + oil systems. The upper temperature limit was extended to about 740 K.

Both the Chao-Seader and Grayson-Streed correlations have been tested with new data. Figures 1 and 2 show a comparison of these correlations with experimental K-values in mixtures of hydrogen and tetralin reported by Simnick et al. (1977). Figure 1 shows that both correlations predict K-values of the solvent quite well. However, Figure 2 shows that neither correlation can do as well for the hydrogen K-values, with that of Chao-Seader in error by about 40% and that of Grayson Streed by about 25%. Similar results have been observed for other systems at comparable temperatures and pressures. There is a clear need for a new correlation for hydrogen.

In this work, we present a correlation of the solubility of hydrogen based on all available phase equilibrium data for hydrogen-containing mixtures of identifiable components at temperatures of 310 to 700 K, and pressures to 30 MPa (300 bar).

SOLUBILITY-PARAMETER-BASED NEW CORRELATION

A new correlation for the solubility of hydrogen has been developed in which the fugacity f of the dissolved hydrogen is expressed as a ratio to its mole fraction x. This ratio (f/x) will be referred to as the undefined activity coefficient, or simply activity coefficient for short, for it differs from the conventional activity coefficient $f/(xf^o)$ by only a factor f^o, the standard state fugacity which is left undefined in this work.

We express the logarithm of the activity coefficient (f/x) of dissolved hydrogen as the sum of a zero-pressure term and a Poynting factor,

$$\ln(f/x) = \ln(f/x)_{p=o} + p\bar{V}/(RT) \tag{1}$$

The zero-pressure activity coefficient is given as a function of the solubility parameter of the solution $\bar{\delta}$, and the temperature T,

$$\ln(f/x)_{p=o} = A_1 + A_2T/\bar{\delta} + A_3T + A_4T\bar{\delta} + A_5T^2\bar{\delta}^2 + A_6(\bar{\delta}/T)^2 \tag{2}$$

The coefficients A are given in Table 1. Fugacity is in bars, T in Kelvins, and δ in $(\text{cal/mL})^{0.5}$.

The solubility parameter of the solution $\bar{\delta}$ is the volumetric average of the component solubility parameters:

$$\bar{\delta} = \left(\sum_i \delta_i V_{ui}\, x_i\right) \Big/ \left(\sum_i V_{ui}\, x_i\right) \tag{3}$$

The component solubility parameter δ is defined as the square root of the energy density of the pure liquid:

$$\delta = \sqrt{\Delta U_v/V} \tag{4}$$

where ΔU_v is the isothermal energy of vaporization into vacuum. Except for hydrogen, the evaluation of δ is by Eq. 4 in this work and is always performed at the system temperature for the

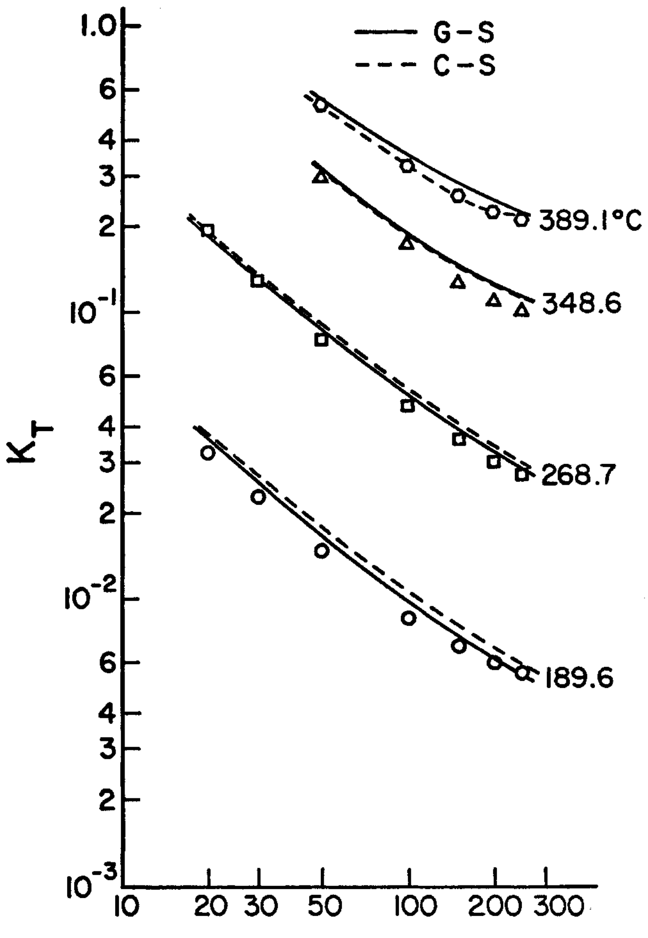

Figure 1. Comparison of K_T data in H_2 + tetralin with Chao-Seader and Grayson-Streed correlations.

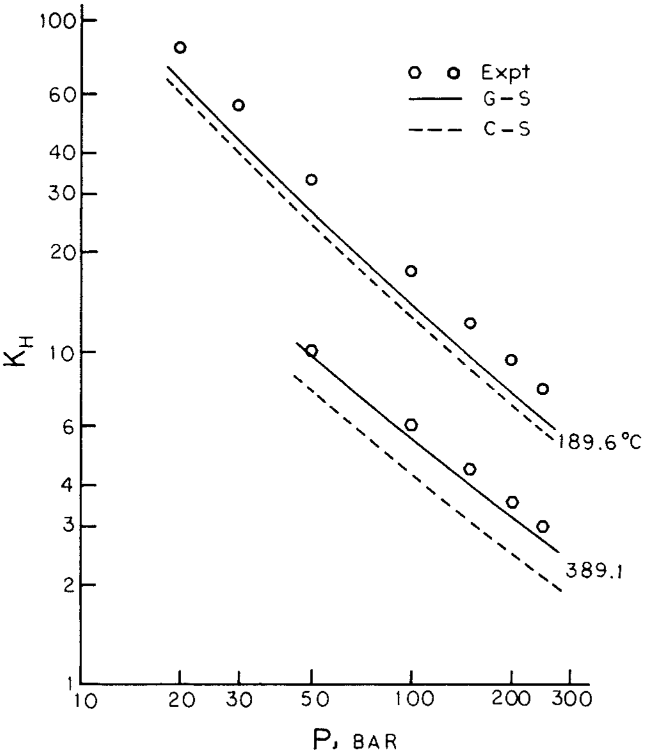

Figure 2. Comparison of K_H data in H_2 + tetralin with Chao-Seader and Grayson-Streed correlations.

TABLE 1. COEFFICIENTS IN EQS. 2 AND 5

Eq. 2 for Activity Coefficient

$A_1 = 5.39456$
$A_2 = -2.8823 * 10^{-3}$
$A_3 = -3.3060 * 10^{-3}$
$A_4 = 1.3117 * 10^{-3}$
$A_5 = -1.0410 * 10^{-7}$
$A_6 = 1117.88$

Eq. 5 for Partial Molal Volume of Hydrogen

$B_1 = -91.813$
$B_2 = 0.4486$
$B_3 = -6.8692 * 10^{-5}$
$B_4 = 13.988$
$B_5 = -0.3780$
$B_6 = -3.7818 * 10^{-2}$

saturated pure liquid, regardless of the total pressure of the system.

The van der Waals volume V_w in Eq. 3 is obtained from group-contribution values given by Bondi (1968) except for hydrogen for which we use the value 10.5 mL/g-mol based on the interatomic distance and the van der Waals radius of the combined hydrogen atoms. The van der Waals volumes of a number of solvents are given in Table 2.

The partial molal volume of dissolved hydrogen that appears in Eq. 1 has been correlated in terms of T and $\bar{\delta}$,

$$\bar{V} = B_1 + B_2T + B_3T^2 + B_4\bar{\delta} + B_5\bar{\delta}^2 + B_6\bar{\delta}\,T \qquad (5)$$

The coefficients B are given in Table 1.

The calculation of solubility parameter is described in Appendix B. To facilitate use of the correlation, we express the variation of the solubility parameter with temperature with

$$\delta = C_1 + C_2T + C_3T^2 + \frac{C_4}{C_5 - T} \qquad (6)$$

The coefficients in Eq. 6 are given in Table 2 for a number of solvents for the entire temperature range of the liquid state. Hydrogen solubility data in these solvents are the basis of the present correlation. Table 2 gives the physical property values that were used in the development of the correlation.

For hydrogen we use the constant δ value 2.33 which is the value at the normal boiling point. Experience from numerous tests shows the correlation results to be insensitive to the value of δ of hydrogen used so long as it is below 3.0.

Seven isotherms of activity coefficient at zero pressure are generated from Eq. 2 and shown in Figures 3 to 9 for comparison with reduced data. Clearly, the reduced data are functions of the solubility parameter of the mixture. The activity coefficient increases as the solubility parameter increases at a fixed temperature, and is completely determined by it except for fine details of variations and for occasional systems that are not well correlated. The figures also show 10% error bounds, and we observe the great majority of reduced data points to be within ± 10% of the equation.

Figure 10 shows that the zero-pressure activity coefficient of Eq. 2 is a slowly varying function of temperature that decreases gradually as temperature rises.

Figure 11 shows the partial molal volume of hydrogen given by Eq. 5. The partial molal volume increases with increasing temperature. At lower temperatures, it is insensitive to solubility parameter, but at higher temperatures it is reduced in solutions of higher solubility parameters. The dependence of partial molal volume on pressure is not considered in this work in the interest of simplicity. Experimental results indicate little dependence on pressure at the lower temperatures but substantial dependence at higher temperatures. The consequence of our not considering pressure as a factor is that the correlated values of partial molal volume correspond to real values at the higher, rather than the lower, pressures in the range of interest. This is because the Poynting factor, the last term of Eq. 1,

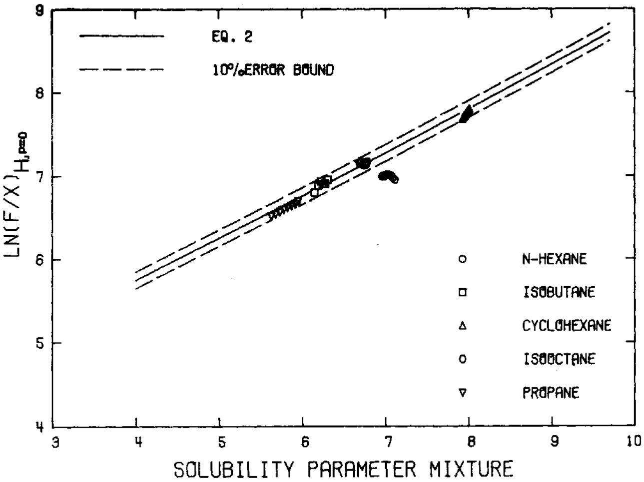

Figure 3. Zero-pressure activity coefficient of hydrogen at 310K.

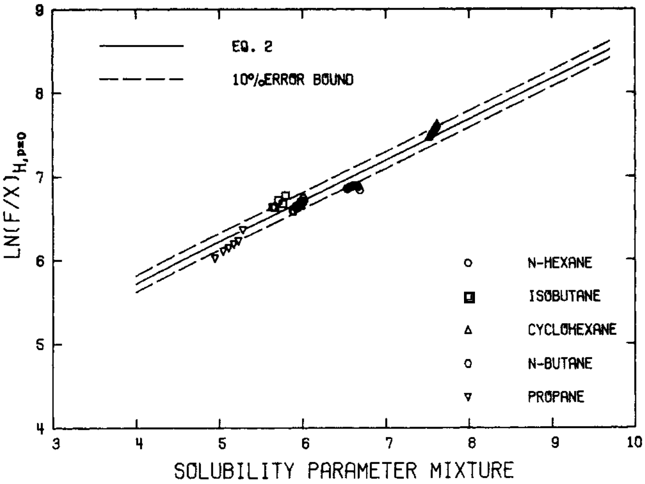

Figure 4. Zero-pressure activity coefficient of hydrogen at 340K.

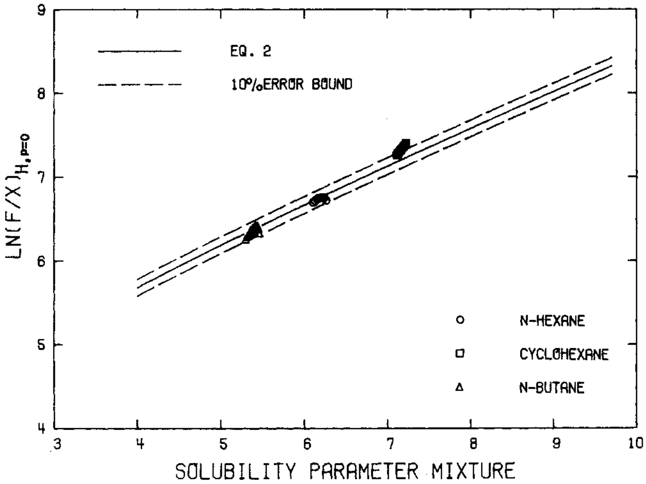

Figure 5. Zero-pressure activity coefficient of hydrogen at 377K.

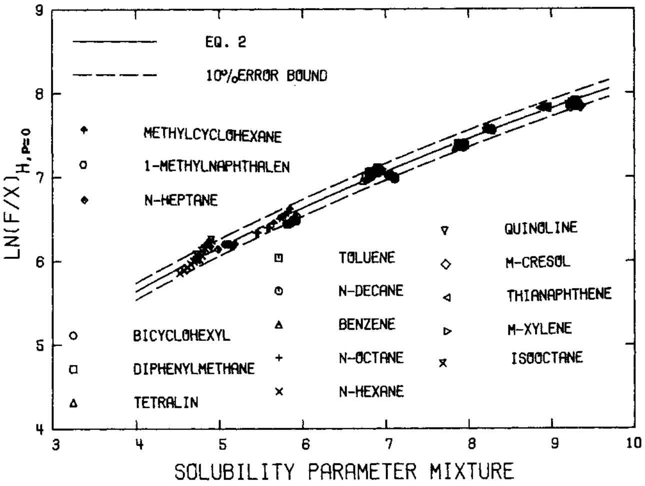

Figure 6. Zero-pressure activity coefficient of hydrogen at 462K.

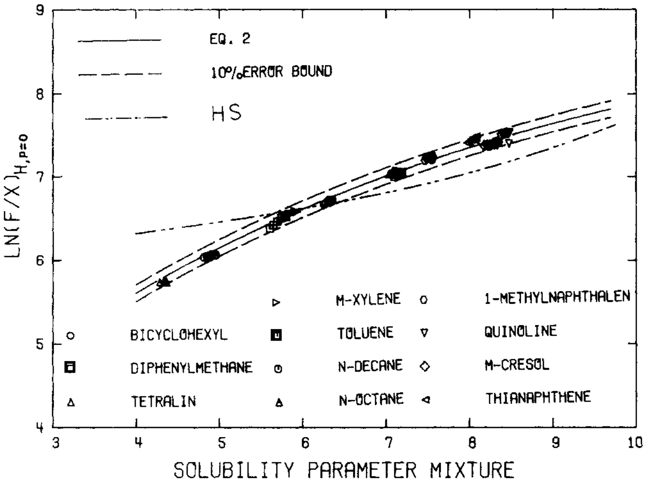

Figure 7. Zero-pressure activity coefficient of hydrogen at 542K.

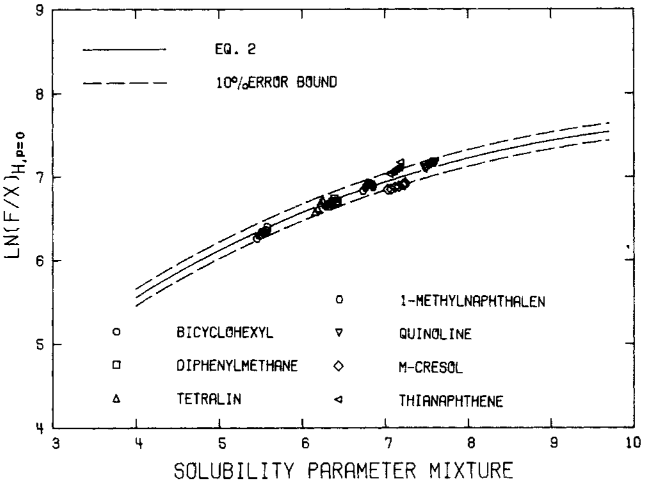

Figure 8. Zero-pressure activity coefficient of hydrogen at 621K.

contributes appreciably only at higher pressures. Our correlated partial molal volume, therefore, serves its function for the purposes of calculating activity coefficients for compressed liquids, but can be in substantial error at the higher temperatures when used for volume calculations at lower pressures.

Table 3 shows the hydrogen partial molal volume in solutions with benzene from Connolly and Kandalic (1963a) and comparable results from Eq. 5. The temperatures in Table 3 are quite high for hydrogen + benzene and the data are sensitive to pressure, especially at the higher temperatures. Eq. 5 corresponds to the data at about 150 atm or higher depending on the temperature.

Lyckman and Eckert (1965) correlated the partial molal volumes of dissolved gases other than hydrogen at infinite dilution against the solubility parameters of the solvents. Eq. 5 represents an extension of the method of Lyckman and Eckert. Brelvi

Table 2. Physical Properties of Pure Compounds

									Constants in Eq. 6		
Compound	p_c bar	V_c mL/mol	T_c K	ω	ΔH_{vb} cal/mol	T_b K	V_{25} mL/mol	V_w mL/mol	C_1	C_2	C_3
Hydrogen	12.97	65.0	33.2					10.5	—	—	—
Propane	42.5	203.0	369.8	0.152	4487	231.1	89.02	37.57	11.098	-1.560×10^{-2}	-1.520×10^{-6}
n-Butane	38.0	255.0	425.2	0.193	5352	272.7	101.44	47.80	10.928	-1.312×10^{-2}	-2.239×10^{-6}
i-Butane	36.5	263.0	408.1	0.176	5090	261.3	105.57	47.80	10.841	-1.317×10^{-2}	-5.788×10^{-6}
n-Hexane	29.7	370.0	507.4	0.296	6896	341.9	131.7	68.26	10.718	-1.056×10^{-2}	-2.538×10^{-6}
n-Heptane	27.4	432.0	540.2	0.351	7576	371.6	149.67	78.49	10.516	-9.304×10^{-3}	-3.584×10^{-6}
n-Octane	24.8	492.0	568.8	0.394	8225	398.9	163.5	88.72	10.566	-8.965×10^{-3}	-3.254×10^{-6}
2-2-4 Trimethylpentane	25.6	468.0	543.9	0.303	7411	372.4	166.2	88.72	9.817	-8.646×10^{-3}	-3.093×10^{-6}
n-Decane	21.6	603.0	617.5	0.490	9388	447.3	196.0	109.18	10.419	-8.2117×10^{-3}	-2.7706×10^{-6}
Cyclohexane	40.7	308.0	553.4	0.213	7160	353.9	108.7	68.26	11.491	-1.058×10^{-2}	-1.416×10^{-6}
Methylcyclohexane	34.8	368.0	572.1	0.233	7440	374.1	127.62	70.47	10.818	-9.261×10^{-3}	-2.234×10^{-6}
Bicyclohexyl	26.1	577.0	731.4	0.388	10963	510.2	186.6	110.86	10.997	-7.470×10^{-3}	-1.406×10^{-6}
Benzene	48.9	259.0	562.1	0.212	7352	353.3	88.81	48.36	12.722	-1.138×10^{-2}	-1.630×10^{-6}
Toluene	41.1	316.0	591.7	0.257	7930	383.8	106.27	59.51	12.198	-1.060×10^{-2}	-1.263×10^{-6}
m-Xylene	35.5	376.0	617.0	0.331	8690	412.3	123.6	65.12	13.715	-1.878×10^{-2}	1.071×10^{-5}
m-Cresol	45.6	312.0	705.9	0.450	11330	475.4	105.07	51.36	14.694	-1.056×10^{-2}	-1.636×10^{-6}
Tetralin	33.5	438.0	716.5	0.316	10575	480.6	136.48	80.98	12.522	-9.819×10^{-3}	3.161×10^{-7}
Thianaphthene	38.8	385.0	752.1	0.283	11070	494.2	116.22	68.94	13.209	-7.832×10^{-3}	-2.816×10^{-6}
1-Methylnaphthalene	35.7	462.0	772.0	0.302	11000	517.8	139.97	85.12	12.598	-9.620×10^{-3}	6.878×10^{-6}
Quinoline	45.6	403.0	782.0	0.333	11888	511.2	118.64	71.10	13.273	-7.038×10^{-3}	-2.754×10^{-6}
Diphenylmethane	29.8	527.0	767.0	0.481	11732	537.5	167.93	98.46	11.880	-7.558×10^{-3}	-1.775×10^{-6}

SI Conversion: bar = kPa × 100.

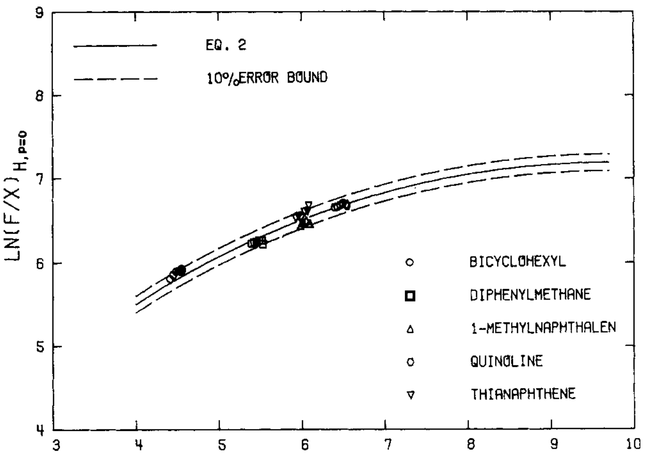

Figure 9. Zero-pressure activity coefficient of hydrogen at 701K.

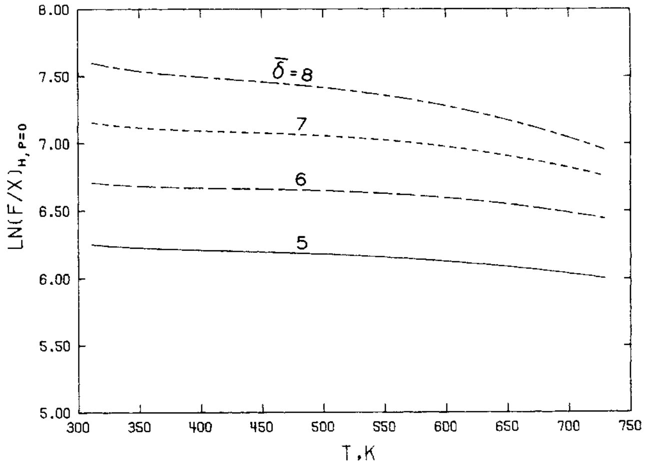

Figure 10. Zero-pressure activity coefficient as a function of temperature.

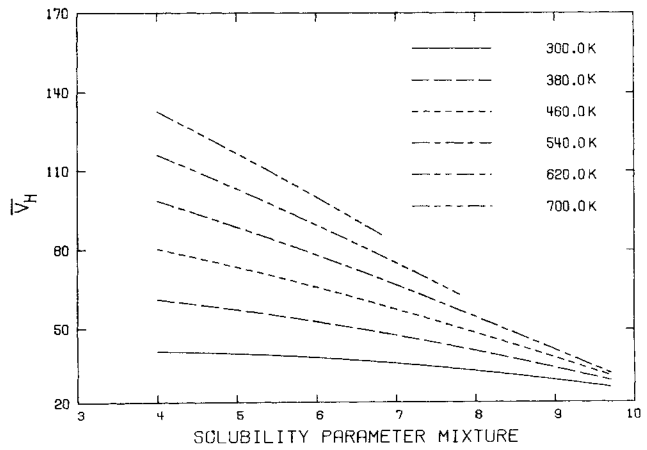

Figure 11. Partial molal volume of dissolved hydrogen by Eq. 5.

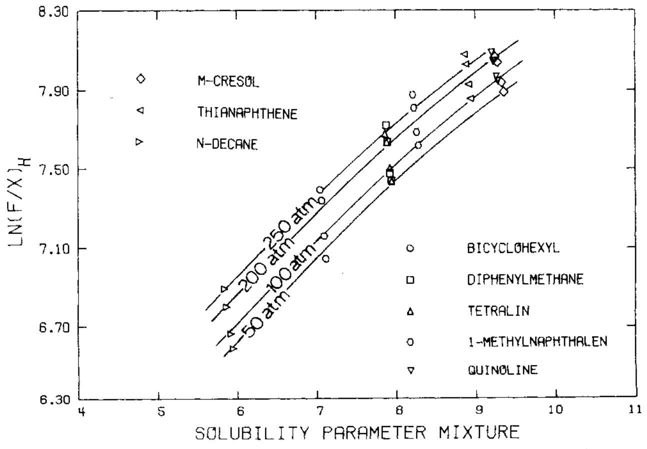

Figure 12. Activity coefficient data in several solvents at 462K.

C_4	C_5
—	—
− 7.813	374.25
− 9.620	431.27
−10.754	415.17
−10.858	514.34
− 9.553	545.53
−12.654	577.32
−10.673	551.14
−14.611	627.08
−11.279	559.80
−10.211	577.78
−34.047	749.43
−14.209	569.90
−16.365	600.88
−55.975	629.37
−25.282	721.94
−25.505	730.77
−11.042	752.00
− 3.530	772.00
−43.317	806.29
−12.240	776.57

and O'Connell (1972) reported a correlation of partial molal volume of dissolved gases also at infinite dilution. Table 4 shows that Eq. 5 is in fair agreement with the Brelvi and O'Connell correlation at the lower temperatures. At the higher temperatures, Eq. 5 always give smaller values corresponding to higher pressures for the reason given above.

DEVELOPMENT OF CORRELATION

In developing the correlation, we first find the fugacity of the dissolved hydrogen by setting it equal to that of hydrogen in the equilibrium gas mixture which is calculated with an equation of state,

$$f_i = \phi_i \, y_i p \tag{7}$$

In this work, the fugacity coefficient ϕ is calculated with the Prausnitz and Chueh (1968) modified form of the Redlich and Kwong (1949) equation of state. A correlation of the binary interaction constant for hydrogen mixtures has been developed for this equation and is described in Appendix A.

The correlation has been developed as a result of investigating the regular solution equation of Scatchard and Hildebrand (Hildebrand, Prausnitz and Scott, 1970):

$$\ln \gamma_i = \frac{V_i \, (\bar{\delta} - \delta_i)^2}{RT} \tag{8}$$

The symmetric activity coefficient γ_H of hydrogen contains in it the fugacity of pure liquid hydrogen f_H^0. Since f_H^0 is not defined by experimental measurements for dissolved hydrogen, we remove it from γ_H and put it on the right hand side of the equation,

$$\ln \, (f_H/x_H)_{p=0} = \frac{V_H(\bar{\delta} - \delta_H)^2}{RT} + \ln f^0_{H,\ p=0} \tag{9}$$

The undefined activity coefficient here has been reduced to zero pressure by means of Eq. 1. According to Eq. 9, the zero-pressure activity coefficient of hydrogen at a fixed T is a function of $\bar{\delta}$ only,

$$\ln \, (f_H/x_H)_{p=0} = F \, (\bar{\delta}, T) \tag{10}$$

The function $F(\bar{\delta}, T)$ is readily established by considering the Henry constant of hydrogen which is defined by:

$$H = \lim_{x_H \to 0} \, (f_H/x_H) \tag{11}$$

TABLE 3. SOME CALCULATED AND EXPERIMENTAL PARTIAL VOLUME OF HYDROGEN IN BENZENE

T, K	p, bar	$\bar{V}^\infty$ mL/g-mol	
		From Connally and Kandalic (1963a)	Eq. 5
473.15	5.51	139.06	
	50.7	108.52	
	101.3	87.06	
	152.0	72.69	72.39
493.15	7.90	188.4	
	50.7	133.96	
	101.3	99.80	
	152.0	79.53	78.25
513.15	10.99	280.08	
	50.7	172.63	
	101.3	115.86	
	152.0	87.19	81.35
533.15	17.33	466.17	
	50.7	238.13	
	101.3	136.59	
	152.0	95.76	91.65

SI Conversion: bar = kPa × 100.

TABLE 4. PARTIAL MOLAL VOLUMES FROM EQ. 5 COMPARED WITH BRELVI AND O'CONNELL CORRELATION

Solvent	T, K	$\bar{V}^\infty$, mL/g-mol	
		Brelvi and O'Connell (1972)	Eq. 5
1-Methylnaphthalene	300	29.7	26.5
	380	32.0	36.2
	460	39.4	45.6
	540	59.0	60.0
	620	94.4	72.2
	700	215.4	98.3
Tetralin	300	29.6	27.5
	380	34.3	36.2
	460	49.0	49.0
	540	76.2	64.9
	620	152.7	85.3
m-Xylene	300	30.6	30.5
	380	44.2	41.7
	540	72.0	57.9
	620	161.4	78.8

The values of H of a gas in various solvents at a given temperature have been shown to be a function of the solubility parameter of the solvent (Hildebrand, Prausnitz and Scott, 1970). Since the saturation pressures of most solvents are practically zero, we see that the F function of Eq. 10 is the same as that of H as a function of δ of the solvents. The difference between the function $F(\bar{\delta}, T)$ thus established, and the experimental (f_H/x_H) data then yields values of partial molal volume according to Eq. 1. The resulting partial molal volumes have been correlated with Eq. 5 and shown in Figure 11.

Figure 12 shows the experimental activity-coefficient data at 462 K for hydrogen dissolved in several solvents. A family of curves seems to be established with pressure as the parameter. This family of curves has been collapsed into the single curve of Figure 6 at $p = 0$ with the use of partial molal volume according to Eq. 1.

Figures 3 to 9 show that the reduced data of activity coefficient at zero pressure are indeed a function of $\bar{\delta}$, as suggested by the regular-solution equation, Eq. 8. However, the regular-solution equation does not give a quantitative representation of the reduced data. In fact, the reduced data show a negative curvature in its isothermal variation with $\bar{\delta}$, while the regular-solution

TABLE 5. COMPARISON OF CORRELATED AND EXPERIMENTAL ACTIVITY COEFFICIENTS FOR HYDROGEN IN BINARY AND TENARY SOLUTIONS

Solvent	T, K	p, bar	No. of points	AAD%	Source
Propane	277/360	34/276	25	8.7	Burriss et al. (1953)
n-Butane	327/394	27/168	60	4.5	Klink et al. (1975)
i-Butane	310/394	34/207	21	12.1	Dean et al. (1946)
n-Hexane	277/310	34/276	16	28.2	Nichols et al. (1957)
	344/477	34/276	40	3.9	
n-Heptane	424/498	24/294	19	6.2	Peter et al. (1960)
n-Octane	463/543	9/125	45	5.6	Connolly (1963b, 1965)
2-2-4-Trimethylpentane	310/423	11/276	20	9.4	Dean et al. (1946)
	424/499	24/294	22	6.6	Peter et al. (1960)
n-Decane	462/583	20/253	26	8.5	Sebastian et al. (1980)
Cyclohexane	310/411	34/276	32	14.1	Berty et al. (1966)
Methylcyclohexane	424/498	24/294	18	4.0	Peter et al. (1960)
Bicyclohexyl	462/701	20/253	28	8.6	Sebastian, Yao (1978)
Benzene	433/533	20/155	49	4.5	Connolly (1962)
Toluene	462/574	20/253	24	4.8	Simnick, Sebastian (1978)
m-Xylene	462/582	20/253	27	2.3	Simnick et al. (1979)
m-Cresol	462/662	20/253	41	8.0	Simnick et al. (1979)
Tetralin	462/662	20/253	23	3.8	Simnick et al. (1977)
Thianaphthene	462/701	20/253	27	7.6	Sebastian, Simnick (1978b)
1-Methylnaphthalene	462/730	20/253	33	3.2	Yao et al. (1977)
Quinoline	462/701	20/253	27	2.3	Sebastian, Simnick (1978a)
Diphenylmethane	462/701	20/253	27	4.0	Simnick (1978)
Diphenylmethane+Tetralin	462/700	20/253	32	4.5	Oliphant et al. (1979)
m-Xylene+Tetralin	462/582	20/253	32	4.3	Oliphant et al. (1979)

SI Conversion: bar = kPa × 100.

equation predicts a positive curvature. Figure 7 shows this difference. A suitable value of f^0 has been used to bring the Hildebrand-Scatchard equation (designated as H.S. in the figure) to line up with the data to the maximum possible extent. Since a large amount of data is available, we have developed the correlation to be based on the data without using the precise form of the Hildebrand-Scatchard equation.

TESTING THE CORRELATION

Table 5 presents a comparison of the correlation with data for hydrogen in various binary and ternary solutions. Included in the table are the temperature and pressure ranges, the number of experimental data points, and the absolute average deviation of the predicted from the experimental activity coefficients, defined by:

$$AAD = \frac{1}{N} \sum_{i}^{N} \frac{|(f_H/x_H)_{\text{exp},i} - (f_H/x_H)_{\text{calc},i}|}{(f_H/x_H)_{\text{exp},i}} \qquad (12)$$

where N is the number of experimental points and i denotes the data point.

The deviations are also shown in Figures 3 to 9 as deviations of the points from the curves; the same deviations would be obtained for K-values of hydrogen if all the factors are calculated as prescribed here, including the fugacity coefficient ϕ in the equilibrium vapor phase. The *AAD* values in Table 5 indicate good agreement for almost all of the systems tested, but the results are especially good for the heavy aromatic hydrocarbon systems. All the absolute average deviations are less than 14% except for hydrogen in hexane at 277 and 310 K. If these two lowest temperatures are neglected, the correlation works as well for *n*-hexane as with the other systems.

As an example of K-values of hydrogen calculated from the new correlation, Figure 13 shows the results for hydrogen in mixtures with tetralin. Good agreement of the calculation with experimental data has been obtained. The vapor-phase calculations are carried out with the equation of state described in Appendix A. The K-value is obtained upon combining the activity coefficient and fugacity coefficient,

$$K = \frac{(f/x)}{p\phi} \qquad (13)$$

Table 6 presents a comparison of the correlation with data for hydrogen in five narrow boiling cuts of coal liquids. The experimental data are taken from Lin et al. (1980). The *AAD*'s are generally comparable to those shown in Table 5. Due to the lack

TABLE 6. COMPARISON OF CORRELATION AND EXPERIMENT FOR HYDROGEN SOLUBILITY IN COAL LIQUIDS

Solvent	T, K	p, bar	No. of points	AAD, %
SRCII #5	462/543	50/253	8	6.6
SRCII #9	463/543	50/253	8	7.7
SRCII #12	542	50/253	4	0.8
EDS CLPP(400-450)	462/622	50/253	9	5.7
EDS CLPP(500-600)	462/543	50/253	8	10.4

SI Conversion: bar = kPa × 100.

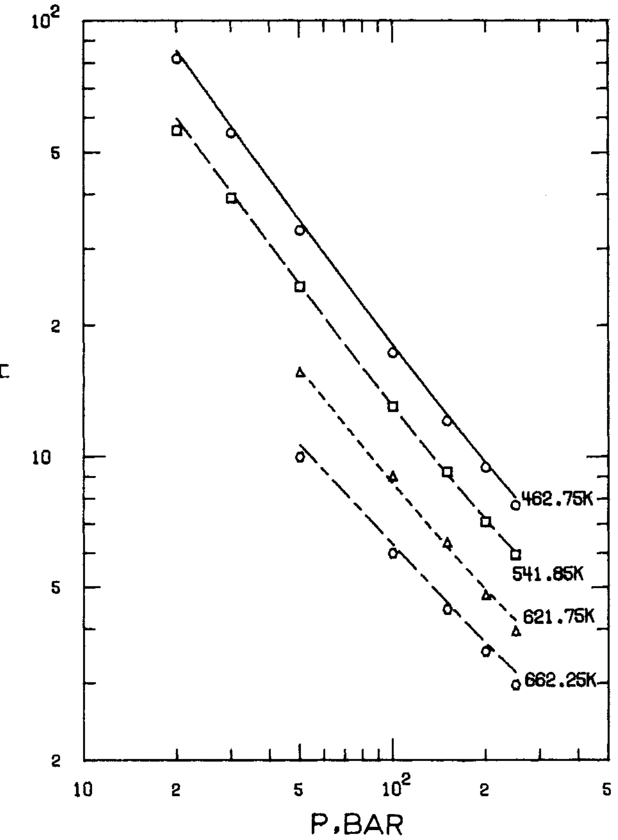

Figure 13. Comparison of K_H data in H_2 + tetralin with new correlation.

of published solubility data of hydrogen in coal oils, an exhaustive test of the correlation is not possible at this time.

The specifications of two of the coal oil fractions were supplied by Exxon Research and Engineering Co. and the other three by Gulf Research and Development Co.; all have been presented by Lin et al. (1980). In Table 7, we report the physical properties we have estimated for the oil fractions for the purposes of calculating the necessary parameters in this work. The values of V_w were calculated from the correlation of the collision diameter for pseudocomponent cuts recommended by API Technical Data Book (1967).

DISCUSSION AND CONCLUSION

Our correlation of solubility of hydrogen is in the form of an undefined activity coefficient without a conventional standard state and the activity coefficient based on it. The results are, nevertheless, readily re-expressed in a conventional form. Thus, in terms of Henry constant and the unsymmetric activity coefficient:

$$(f/x)_{p=o} = H\,\gamma^* \tag{14}$$

we would have

$$\ln H = F|_{\bar{\delta}=\delta \text{ of solvent}} \tag{15}$$

and

$$\ln \gamma^* = F|_{\bar{\delta}} - F|_{\bar{\delta}=\delta \text{ of solvent}} \tag{16}$$

where the F function is given by Eq. 2.

In terms of a hypothetical pure liquid hydrogen and the symmetric activity coefficient:

$$(f/x)_{p=o} = f_L^0\,\gamma \tag{17}$$

we would have

$$\ln f_L^0 = F|_{\bar{\delta}=2.33} \tag{18}$$

and

$$\ln \gamma = F|_{\bar{\delta}} - F|_{\bar{\delta}=2.33} \tag{19}$$

Both factors H and γ^* in the unsymmetric convention are given meaningful values in Eqs. 15 and 16. However, the separate values of f_L^0 and γ from Eqs. 18 and 19 depend on a long extrapolation of Eq. 2 to a low value of δ.

We have bypassed the conventions in the interest of convenience. The same method is applicable to the solubilities of other gases and we are developing correlations for several.

The present correlation for hydrogen has been shown to be of reasonable accuracy and high reliability. It is believed to be useful for engineering calculations.

TABLE 7. CALCULATED PHYSICAL PROPERTIES OF COAL LIQUIDS

	P_c bar	V_c mL/mol	T_c K	ω	ΔH_{vb} cal/mol	V_w mL/mol
SRCII #5	30.23	628.2	754.5	0.4055	11818	94.5
SRCII #9	26.58	720.8	822.7	0.5093	12725	143.4
SRCII #11	25.69	840.7	882.8	0.4049	13859	141.3
EDS CLPP(400-450)	31.64	542.6	703.2	0.5211	10218	91.1
EDS CLPP(500-600)	26.54	628.4	783.1	0.550	12070	172.5
Calculation Method	Lee & Kessler (1976)	Hall & Yarborough (1971)	Lee & Kessler (1976)	Edmister (1961)	Vetere (see Reid, Sherwood, Prausnitz (1977))	A.P.I. Technical Data Book (1967)

SI Conversion: bar = kPa × 100.

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APPENDIX A: CALCULATION OF FUGACITY COEFFICIENT OF HYDROGEN

In this work the vapor-phase fugacity coefficient of hydrogen is calculated from the Prausnitz and Chueh (1968) modification of the Redlich-Kwong (1949) equation of state:

$$\left[P + \frac{a}{T^{0.5}V(V+b)}\right][V - b] = RT \tag{A-1}$$

with the constants

$$a = \sum_i \sum_j y_i y_j a_{ij} \tag{A-2}$$

and

$$b = \sum_i y_i b_i \tag{A-3}$$

where

$$a_i = \frac{\Omega_{ai}\, R^2 T_{ci}^{2.5}}{P_{ci}} \tag{A-4}$$

$$b_i = \frac{\Omega_{bi}\, RT_{ci}}{P_{ci}} \tag{A-5}$$

and the cross term

$$a_{ij} = \frac{(\Omega_{ai} + \Omega_{aj})R^2 T_{cij}^{2.5}}{2\, P_{cij}} \tag{A-6}$$

Here, the Ω_{ai} are constants for each component and T_{cij} and P_{cij} are given by:

$$T_{cij} = (1 - k_{ij})\,(T_{ci} * T_{cj}^{0.5}) \tag{A-7}$$

where k_{ij} is the interaction constant based on a geometric mean rule, and

$$P_{cij} = Z_{cij}\, RT_{cij}/V_{cij} \tag{A-8}$$

V_{cij} is given by the arithmetic average

$$V_{cij} = \frac{V_{ci} + V_{cj}}{2} \tag{A-9}$$

and Z_{cij} is given by the relation

$$Z_{cij} = 0.291 - 0.04\,(\omega_i + \omega_j) \tag{A-10}$$

There are two constants Ω_a and Ω_b for each component which must be determined, as well as one constant, k_{ij}, for each binary pair. Prausnitz and Chueh (1968) reported the values of Ω_a and Ω_b for 19 pure substances, and these values were correlated by Yao and coworkers (1977) in terms of the acentric factor ω. Yao's correlations are used in this work. The interaction constants k_{ij} were determined for a group of mixtures by fitting the equation of state to the fugacity coefficient of the solvents:

$$\phi_s = \frac{\phi_s^o\, p_s^o\, x_s \exp \dfrac{V_s p}{RT}}{P y_s} \tag{A-11}$$

where ϕ_s^o is the fugacity coefficient of the saturated vapor which is taken from Chao and Greenkorn (1975), p_s^o is the vapor pressure and V_s is the liquid molar volume.

Values of k_{ij} so obtained have been correlated against the critical volume of the solvents:

$$k_{ij} = 0.00015\, V_{cs} - 0.0275 \tag{A-12}$$

These generalized constants were then used in the Prausnitz-Chueh equation to calculate vapor fugacity coefficients for the systems H_2/butane and H_2/benzene. The fugacity coefficients determined from the equation are compared to those reported by Klink et al. (1975) and Connolly (1962) in Tables A-1 and A-2. Although neither of these systems was used in fitting the constants, agreement between the calculated and experimental values is excellent. The average difference in ϕ_H for the H_2/butane system is 1.2% and for the H_2/benzene system it is 0.64%. The average difference for ϕ_s in the H_2/benzene system is 1.8%.

TABLE A-1. COMPARISON OF ϕ_H FOR H_2 + n-BUTANE SYSTEM

T, K	p, bar	ϕ_H calc	ϕ_H exp
327.7	31.27	1.0478	1.0493
	42.54	1.0482	1.0478
	55.85	1.0518	1.0488
	68.69	1.0585	1.0522
	83.76	1.0656	1.0587
	92.48	1.0702	1.0620
	104.31	1.0769	1.0671
	117.42	1.0847	1.0732
	130.31	1.0921	1.0787
	138.04	1.0970	1.0817
	138.21	1.0968	1.0823
	157.77	1.1091	1.0923
	168.47	1.1161	1.0978
344.3	27.78	1.0810	1.0889
	41.77	1.0715	1.0752
	54.97	1.0711	1.0729
	69.30	1.0739	1.0721
	83.46	1.0792	1.0754
	96.79	1.0853	1.0798
	106.28	1.0886	1.0826
	111.01	1.0907	1.0832
	124.64	1.0991	1.0900
	139.81	1.1078	1.0968
	150.84	1.1149	1.1028
	166.53	1.1255	1.1117
361.0	27.93	1.1475	1.1667
	41.17	1.1207	1.1324
	56.17	1.1042	1.1129
	68.09	1.1054	1.1094
	83.19	1.1096	1.1115
	98.68	1.1118	1.1111
	110.85	1.1157	1.1133
	123.56	1.1214	1.1176
	138.47	1.1290	1.1236
	149.97	1.1368	1.1304
	167.88	1.1499	1.1421
377.6	28.34	1.2566	1.2958
	41.74	1.2102	1.2356
	54.03	1.1876	1.2061
	65.68	1.1756	1.1902
	77.78	1.1690	1.1806
	90.25	1.1648	1.1739
	103.21	1.1654	1.1728
	117.64	1.1687	1.1740
	128.59	1.1733	1.1775
	141.40	1.1868	1.1911
	154.61	1.1970	1.2006
	167.38	1.2111	1.2149
394.3	34.31	1.4713	1.5446
	48.62	1.3766	1.4226
	61.46	1.3492	1.3868
	77.17	1.3201	1.3513
	88.65	1.3014	1.3283
	101.50	1.2922	1.3165
	112.87	1.2912	1.3140
	124.72	1.2856	1.3069
	138.91	1.3066	1.3297
	138.99	1.3051	1.3280
	152.89	1.3415	1.3683
	168.76	1.4081	1.4446

SI Conversion: bar = kPa × 100.

APPENDIX B: CALCULATION OF SOLUBILITY PARAMETER

The solubility parameter of a solvent is calculated for the saturated pure liquid according to the defining equation:

Table A-2. Comparison of ϕ for H_2 + Benzene System

		ϕ_H		ϕ_S	
T, K	p, bar	calc	exp	calc	exp
433.15	20.94	1.060	1.066	0.820	0.804
	32.38	1.049	1.053	0.805	0.788
	52.12	1.048	1.049	0.794	0.778
	90.18	1.058	1.058	0.785	0.767
	115.11	1.069	1.067	0.783	0.764
443.15	19.00	1.088	1.097	0.811	0.796
	25.88	1.071	1.077	0.796	0.780
	40.30	1.059	1.063	0.778	0.762
	65.79	1.058	1.059	0.767	0.751
	117.13	1.074	1.073	0.759	0.739
	152.19	1.089	1.086	0.760	0.737
453.15	23.13	1.103	1.112	0.787	0.773
	31.80	1.084	1.090	0.769	0.754
	49.99	1.071	1.074	0.750	0.735
	83.15	1.070	1.071	0.739	0.723
	153.71	1.094	1.092	0.734	0.711
463.15	22.47	1.140	1.154	0.778	0.763
	28.07	1.120	1.131	0.760	0.744
	38.89	1.098	1.106	0.741	0.724
	61.91	1.064	1.088	0.720	0.702
	105.58	1.086	1.087	0.709	0.688
473.15	33.95	1.140	1.151	0.732	0.717
	47.46	1.116	1.123	0.710	0.695
	76.80	1.100	1.103	0.688	0.671
	135.78	1.106	1.107	0.676	0.655
483.15	32.42	1.193	1.207	0.723	0.710
	40.94	1.165	1.176	0.702	0.688
	57.96	1.136	1.143	0.677	0.664
	95.75	1.119	1.122	0.653	0.639
	178.03	1.134	1.134	0.642	0.622
493.15	38.72	1.225	1.239	0.693	0.682
	49.37	1.193	1.203	0.669	0.658
	70.93	1.160	1.166	0.642	0.631
	120.78	1.144	1.146	0.616	0.603
503.15	46.24	1.264	1.278	0.661	0.652
	59.70	1.217	1.237	0.633	0.624
	87.49	1.190	1.196	0.603	0.594
	155.94	1.177	1.178	0.574	0.562
513.15	37.21	1.413	1.437	0.684	0.677
	55.51	1.313	1.326	0.624	0.617
	72.67	1.269	1.278	0.594	0.586
	109.53	1.228	1.233	0.559	0.552
523.15	35.83	1.581	1.613	0.694	0.690
	48.87	1.499	1.451	0.651	0.647
	86.66	1.310	1.317	0.559	0.556
	141.96	1.281	1.284	0.508	0.503
533.15	41.58	1.722	1.751	0.664	0.662
	82.67	1.461	1.468	0.535	0.533
	114.70	1.402	1.406	0.493	0.492

SI Conversion: bar = kPa × 100.

$$\delta = \left(\frac{\Delta U_v}{V}\right)^{0.5} \tag{B-1}$$

where V is the liquid molal volume as calculated from the Gunn and Yamada correlation (1971) and ΔU_v is the isothermal internal energy of vaporization to the ideal-gas state:

$$\Delta U_v = \Delta H_v + (H^o - H) - RT + PV \tag{B-2}$$

where ΔH_v is the heat of vaporization calculated from the Watson equation. The enthalpy departure ($H - H^o$) is from the work of Yen and Alexander (1965). Solubility parameters calculated in this way were used to determine the coefficients in Eq. 6.

NOTATION

f = fugacity
H = enthalpy
H = Henry constant
K = vaporization equilibrium ratio
k = interaction constant
p = pressure
R = gas constant
T = temperature
V = molar volume
x = liquid-phase mole fraction
y = vapor-phase mole fraction
z = compressibility factor
δ = solubility parameter
γ = liquid-phase activity coefficient
ϕ = vapor-phase fugacity coefficient
ω = acentric factor

Subscripts

b = at normal boiling point
c = critical property
calc = calculated
w = van der Waals volume
exp = experimental
H = hydrogen
i, j = components
L = liquid phase
HS = from Hildebrand-Scatchard equation
S = solvent
T = tetralin
25 = at 25°C
v = vaporization property

Superscripts

$*$ = unsymmetric convention activity coefficient
o = reference state
∞ = infinite dilution

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Simultaneous Measurement of Size and Velocity of Bubbles or Drops: A New Optical Technique

Accurate information on both the size and velocity of a dispersed phase is of importance to many problems in heat or mass transfer and reaction. Existing experimental methods are limited in their applicability, difficult to use, provide only size or velocity, and are of low statistical reliability. A new method is developed here which overcomes most of these shortcomings and permits accurate simultaneous measurement of the size and two dimensional velocity of the dispersed phase.

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SCOPE

Knowing the size and velocity distribution of a dispersed phase is important to the prediction of heat and mass transfer as well as chemical reaction in many processes. Situations of industrial importance include spray absorbers, driers and combustors, bubble columns, thermosyphon reboilers, pipeline reactors, condensers operating in annular two-phase flow, as well as in spray cooling systems. Improvement in theoretical understanding of dispersed phase flows and transfer processes has been seriously limited by the paucity of reliable data by which to test new ideas. Thus, the objective of this research has been to devise a new method for making reliable simultaneous measurements of the size and velocity of two coordinate directions of the dispersed phase.

The earliest and still the most widely used methods of measurement are based on photography. Even with modern image analysis equipment and massive numbers of photographs, it is seldom possible to obtain statistically reliable data by photographic techniques except at great expense. Furthermore, two coordinate velocities are almost impossible to measure photographically.

The most recent methods for velocity are based on the use of crossed or reference laser beams and apply principles of laser doppler velocimetry. Measurement of velocity by this technique is well established as long as the dispersed-phase diameter is small enough to result in Mie scattering of the incident light. For air-water, this means drops or bubbles smaller than

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