Correlation of Vapor-Liquid Equilibrium Ratio of Hydrogen

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In this work the correlation of vapor-liquid equilibrium ratio of hydrogen in the Chao-Seader correlation is updated with the use of new experimental data that have appeared in the intervening years. The correlation is extended in the direction of high temperature where much new data have been reported over a wide pressure range.

The hydrogen correlation in the Chao-Seader correlation (Chao and Seader, 1961) was based on experimental data in the temperature range of approximately 200–530 K that was the full extent of available data at the time. Grayson and Streed (1963) extended the hydrogen correlation to higher temperature using proprietary data on oil fractions. Since then a great deal of experimental investigation has been performed to determine the solubility of hydrogen at temperatures up to 730 K and pressure up to 25 MPa. Sebastian and coworkers (1981) developed a correlation for the solubility of hydrogen based on the expanded database. In this work we develop a new equation for the standard state liquid fugacity of hydrogen based on the expanded current database. The new equation will be useful to replace the equation for ν of hydrogen in the Chao-Seader correlation that is found in process design software packages.

Liquid Fugacity Equation

In the Chao-Seader correlation, vaporization equilibrium ratio is given by:

$$K_i = \nu_i \gamma_i / \phi_i \tag{1}$$

where $K_i = y_i/x_i$; ν_i is the standard liquid fugacity coefficient; γ_i is the activity coefficient of i in liquid solution; and ϕ_i is the fugacity coefficient of i in gas mixture.

Values of ν for correlation development is obtained from experimental K_i by rewriting Eq. 1.

$$\nu_i = K_i \phi_i / \gamma_i \tag{2}$$

All three factors on the righthand side of Eq. 2 are calculated from experimental data according to equations in the Chao-Seader correlation: $K_i = y_i/x_i$; γ_i by Scatchard-Hildebrand equation; and ϕ_i by Redlich-Kwong equation of state. Material parameters reported by Chao and Seader (1961) are used in the calculation for ϕ and γ in this work. Solubility parameters are evaluated for the correlation development for substances that were not found in the Chao-Seader correlation: 1-methylnaphthalene, 9.78 $(\text{cal/cm}^3)^{0.5}$; tetralin, 9.07; diphenylmehtane, 9.52. Solubility parameters are revised based on heat of vaporization given by Yaws (1992) for n-decane to 7.64 $(\text{cal/cm}^3)^{0.5}$; and n-hexadecane to 7.57.

Table 1 shows the new experimental data that are added to the old set used in the development of original Chao-Seader correlation. The new data set extends the temperature up to about 730 K. The upper limit of pressure to 25 MPa remains unchanged.

The ν values generated from the data set according to Eq. 2 are correlated as a function of reduced temperature T_r and reduced pressure P_r of hydrogen. The use of reduced T and P is not necessary, but conforms to the usage in the total correlation scheme. The new equation obtained is as follows:

$$\log \nu_H = 0.8669098 + 9.9195929/T_r - 31.4141598/T_r^2 + 37.4500656/T_r^3 + (0.0183734 - 0.1460381/T_r + 0.8545416/T_r^2 - 1.1687170/T_r^3)P_r - 0.0000691 P_r^2 - \log P_r \tag{3}$$

Table 1. Experimental Hydrogen Solubility Data Used in this Work

Solvent	Temp. K.	Pres. MPa	Sources
Toluene	461-575	< 26	Simnick et al. (1978a)
n-Hexadecane	461-664	< 26	Lin et al. (1980)
m-Xylene	462-582	< 26	Simnick et al. (1979)
Bicyclohexyl	462-702	< 26	Sebastian et al. (1978)
n-Decane	462-584	< 26	Sebastian et al. (1980)
1-Methylnaphthalene	462-731	< 28	Yao et al. (1978)
1,2,3,4-Tetrahydro-naphthalene	462-662	< 26	Simnick et al. (1977)
Diphenylmethane	462-702	< 26	Simnick et al. (1987b)

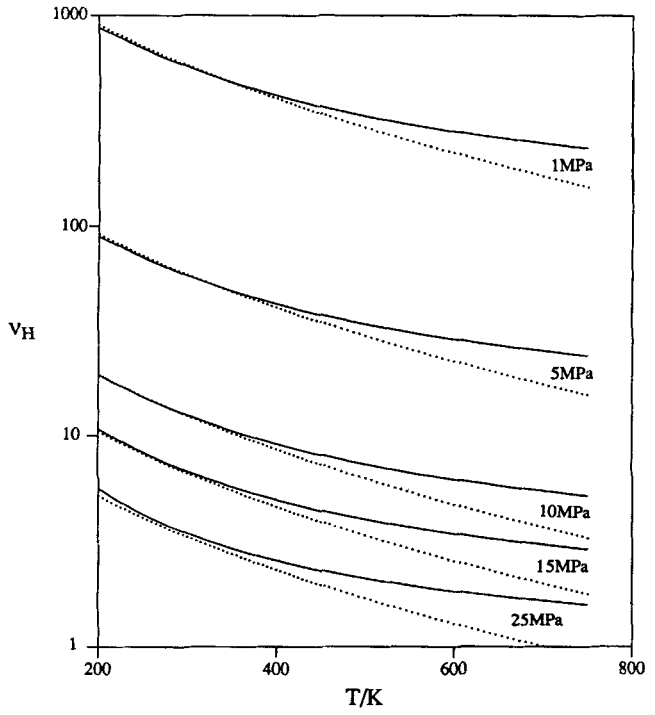

Figure 1. Liquid fugacity coefficient of hydrogen.

(——) new correlation; (·····) original equation.

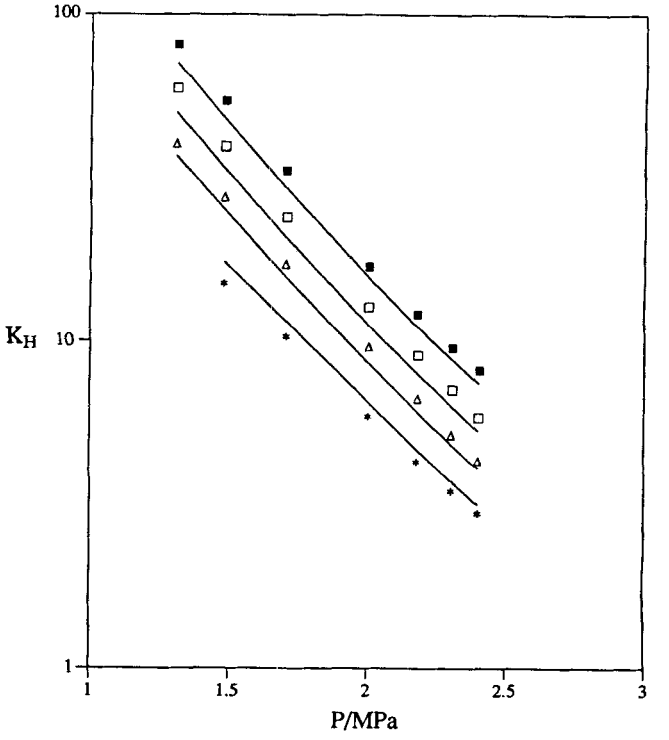

Figure 2. Comparison of new correlation (——) with experimental K (point) of hydrogen in mixture with diphenylmethane.

(■) 462.75; (□) 541.85; (△) 621.75; (*) 701.65 K.

Figure 1 shows the new ν function varying with temperature at several fixed pressures. The original ν function is shown as dotted lines on the figure. The two equations merge together at lower temperatures but diverge at higher temperatures. The gentle steady slope of the new curves at the high temperature range suggests success of reasonable extrapolation to higher temperature.

Comparison of Correlation with Data

The average absolute deviation of Eq. 3 from the ν value data is 8.9%; the average absolute deviation of the original ν equation from the same set of ν values is 14.14%. These are also the deviations from experimental data of the hydrogen K-value correlations based on the ν functions since the factors γ and ϕ are unaltered in either K or ν calculation.

Figure 2 shows comparison of the calculated K_H compared with experimental data in mixtures of hydrogen + 1-methylnaphthalene. Figure 3 shows the original correlation compared with the same data, and this correlation is generally too low.

Similarly the new and original correlations are compared with experimental K_H in mixtures of hydrogen + bicyclohexyl in Figures 4 and 5. Again, the original correlation tends to be low at all the pressures that are observed.

Conclusion

The correlation for vapor-liquid equilibrium ratios of hydrogen in the Chao-Seader correlation is extended to higher temperature (about 730 K), while maintaining about the same useful pressure range. The new correlation is not significantly

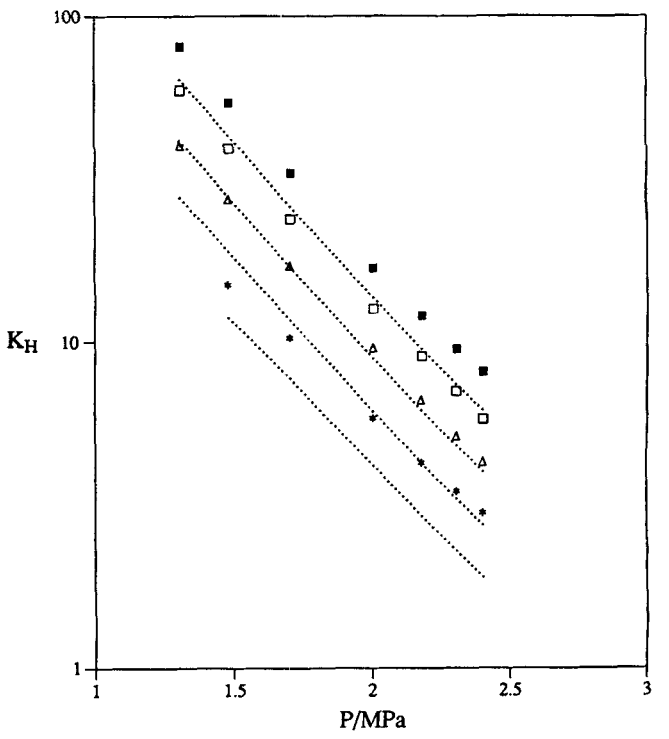

Figure 3. Comparison of original correlation (· · · ·) with experimental K (point) of hydrogen in mixture with diphenylmethane.

(■) 462.75; (□) 541.85; (△) 621.75; (*) 701.65 K.

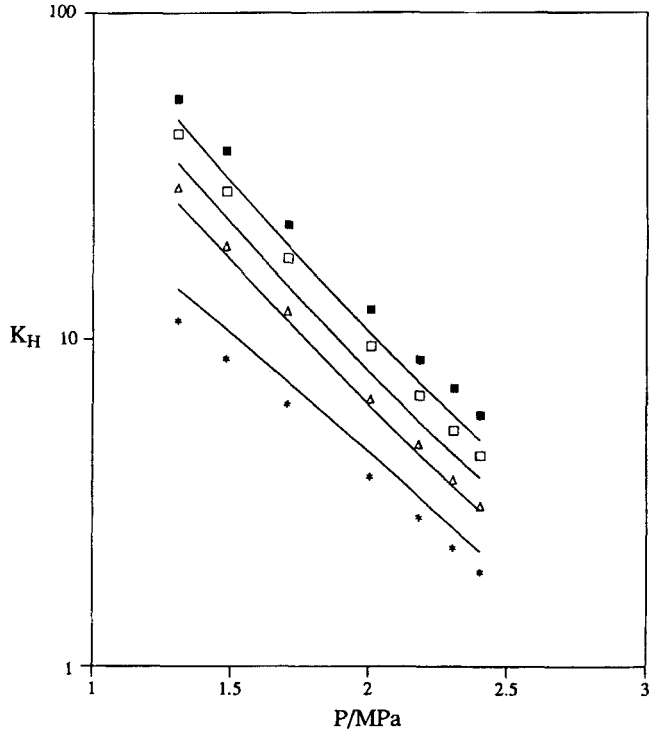

Figure 4. Comparison of new correlation (——) with experimental K (point) of hydrogen in mixture with bicyclohexyl.

(■) 462.75; (□) 541.85; (△) 621.75; (*) 701.65 K.

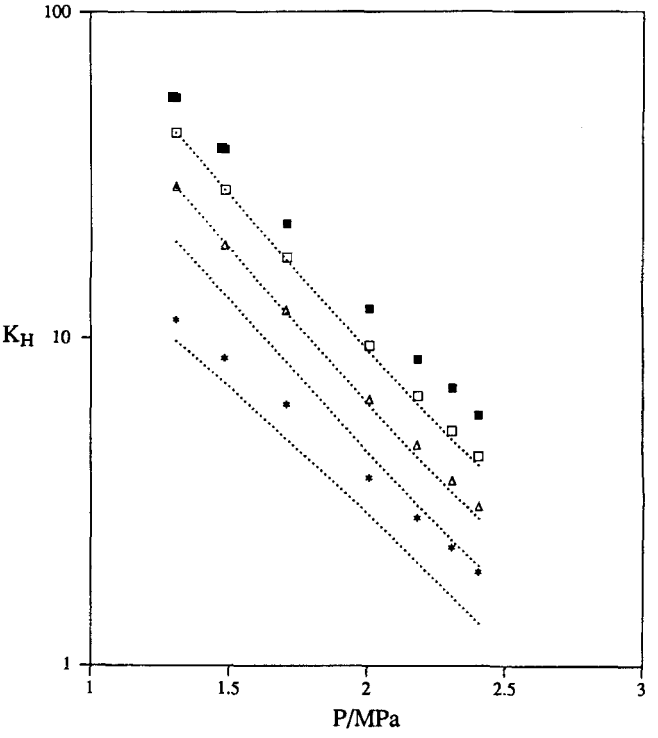

Figure 5. Comparison of original correlation (· · · ·) with experimental K (point) of hydrogen in mixture with bicyclohexyl.

(■) 462.75; (□) 541.85; (△) 621.75; (*) 701.65 K.

altered from the original at lower temperatures, but diverges from it at higher temperatures where the original equation is extrapolated. The gentle steady slope of the new equation at the high temperature range suggests success of reasonable extrapolation to higher temperatures that can be of interest in future hydrofining processes.

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