Solubility of Hydrogen in Pyrolysis Gasoline

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The solubility of hydrogen in pyrolysis gasoline (pygas) was measured within a temperature range of (298 to 343) K and pressures up to 6.0 MPa. The experimental method was validated by comparing the measured hydrogen solubilities in benzene and toluene with published data. The results showed that Henry's law was applicable in the range of operating conditions investigated. Moreover, the hydrogen solubilities in benzene, toluene, BTXS (a mixture composed of benzene, toluene, xylene, and styrene), and pygas increased not only with temperature and pressure, but also with the increase in the molecular weight. The steric effect of the alkyl group of monoaromatics on the hydrogen solubility was remarkable. The Soave−Redlich−Kwong cubic equation of state with the binary interaction parameters was used to predict the hydrogen solubility.

Introduction

Pyrolysis gasoline (pygas), which is a byproduct of the high-temperature naphtha pyrolysis in olefin plants, is characterized by a high content of aromatics such as benzene, toluene, and xylene (BTX), and unsaturated components such as olefins and dienes.[1] These unstable components prevent hydrodesulfurization of sulfur-containing compounds at high temperature. To recover BTX, pygas is first pretreated in three columns to obtain the C_6 to C_8 cut and then is sent to a two-stage hydrogenation process to eliminate olefins and sulfur compounds.[2] The first-stage reactor is used for selective hydrogenation of diolefins to monoolefins, while the second-stage reactor converts the monoolefins and sulfur compounds at high temperature.

The first-stage hydrogenation is performed under mild temperature in a trickle-bed reactor, wherein hydrogen and liquid components flow concurrently downward over the catalyst pellets. It is well-known that hydrogen is dissolved first and then reacts with other reactants on the catalyst. Therefore, the knowledge of the hydrogen concentration in pygas is very important for studying the kinetics of selective hydrogenation of diolefins. However, there are only few studies related to petroleum products. Ronze et al.[3] studied the solubility of hydrogen in straight run gasoil using a chromatographic method. Liu and Que.[4] measured the hydrogen solubilities in atmospheric gasoil, vacuum gasoil, and atmospheric residue. Unfortunately, theoretical studies were not presented. As far as hydrogen solubility in pygas is concerned, few results have been reported so far.

The purpose of this study is to measure the solubility of hydrogen in pygas under experimental conditions similar to those in the first-stage reactor. Furthermore, the Soave−Redlich−Kwong (SRK) equation of state is used to describe the vapor−liquid equilibria in hydrogen−hydrocarbon systems including benzene, toluene, and pygas. Results calculated with the SRK equation are compared with the experimental data measured.

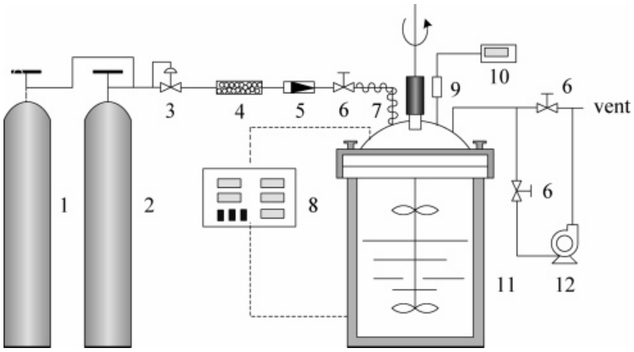

Figure 1. Schematic diagram of the experimental apparatus. 1, hydrogen; 2, nitrogen; 3, pressure regulator; 4, dehydrator; 5, check value; 6, valve; 7, preheater; 8, controller; 9, pressure sensor; 10, manometer; 11, autoclave; 12, vacuum pump.

Experimental Section

The experimental setup is given schematically in Figure 1. Experiments were conducted in a 600 cm^3 autoclave equipped with a magnetic stirrer. The autoclave was connected with a highly resolving pressure sensor (0 to 10) MPa, which was used to monitor variations of the pressure drop in the autoclave. The pressure sensor (Hong Kong Wide Plus Precision Instruments Co., model Wide Plus-8) had an accuracy of ± 0.1 % of full scale. The autoclave was well-insulated, and variations in temperature between vapor and liquid were less than 0.5 °C. The temperature was measured by a calibrated Nichrome nickel−copper thermocouple (0 to 600) °C (Shanghai Automation Instruments Co., model WREK-101), which had an accuracy of ± 0.5 °C by comparison with a platinum resistance thermometer.

The uncertainty of this measurement for the hydrogen solubility in pygas mostly depends on the uncertainty of the measured variables such as temperature, pressure, and volume of the solvent, and it may be considered to be within 2 %. The volume of the solvent is measured by a graduated cylinder, and its uncertainty is 1 %. The total uncertainty of temperature and pressure is not larger than 1 %.

The autoclave filled with 400 cm^3 solvent was first degassed with a vacuum pump for half an hour at room temperature. A

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Table 1. Density ρ, Molar Mass M, and Mass Fraction w of Benzene (1) + Toluene (2) + Xylene (3) + Styrene (4)

property	value
ρ at 293 K/g·cm^{-3}	0.8724
M/g·mol^{-1}	86.51
100 w_1	50.0
100 w_2	30.0
100 w_3	10.0
100 w_4	10.0

Table 2. Density ρ, Molar Mass M, and Mass Fraction w of Pygas

property	value
ρ at 293 K/g·cm^{-3}	0.8535
M/g·mol^{-1}	88.36
100 w_1	47.0
100 w_2	22.8
100 w_3	9.3
100 w_4	7.5
100 w_5 [a]	2.4
100 w_6	1.0
100 w_7	0.9
100 w_8	1.9
100 w_9	1.0
100 w_{10}	6.1

[a] w_5, w_6, w_7, w_8, w_9, and w_{10} denote mass fractions of ethylbenzene, cyclopentadiene, hexane, 3,3-dimethylpentane, 2,2,3-trimethylbutane, and other components remaining, respectively.

liquid sample of about 1 cm^3 was taken from the autoclave and analyzed by gas chromatography to check whether the mixture composition was changed after degassing. It showed that the mixture compositions before and after degassing were almost identical. The autoclave was heated to the desired temperature under N_2 protection, and then, it was purged with preheated hydrogen for four times to exclude N_2. Almost all the nitrogen was substituted by hydrogen according to the analysis of the gas sample by gas chromatography. Hydrogen was used to pressurize the autoclave. When the desired pressure was reached, the hydrogen feed was stopped. Meanwhile, the stirrer was engaged, and the data collection started.

The measurements are based on an isochoric method, i.e., the pressure drop is monitored under constant-volume conditions. This method is described in detail by Ledakowicz et al.[5] The hydrogen solubility x in different hydrocarbons, which is defined as the mole fraction of hydrogen in the liquid phase, can be calculated by

$$x = n_H/(n_H + n_L) \tag{1}$$

where n_H and n_L are the moles of hydrogen and solvent in the liquid phase, which are given by

$$n_H = \frac{V_G(P_0 - P_f)}{RT} \tag{2}$$

$$n_L = \rho_L V_L/M_L \tag{3}$$

where M_L, V_L, and ρ_L are, respectively, the molar mass, the volume, and the density of the solvent, V_G is the volume of the gas phase, and P_0 and P_f are, respectively, the initial pressure (at $t = 0$) and the steady-state pressure. Four different systems are investigated in this study, i.e., benzene, toluene, benzene + toluene + xylene + styrene (BTXS), and pygas. BTXS is prepared in the laboratory, while pygas is collected from a pygas hydrogenation unit of SINOPEC Yangzi Petrochemical Company Limited. The properties of BTXS and pygas are presented in Tables 1 and 2, respectively.

Pygas is a complex liquid, which is composed of many different hydrocarbons. Table 2 lists the nine main components in pygas and other residual components, each of which has a mass fraction no higher than 0.5 %. Experiments are carried out over a temperature range of (298 to 343) K, within which the industrial first-stage reactor is practically operated.

Materials. Benzene, toluene, xylene, and styrene were supplied by Sinopharm Group Chemical Reagent Co. and had purities of 99.5 %, 99.5 %, 99 %, and 99 %, respectively. All materials were used without further purification.

SRK Equation of State

The Soave modification of the Redlich−Kwong (RK) equation of state is given as follows

$$P = \frac{RT}{v - b} - \frac{\alpha a}{v(v + b)} \tag{4}$$

where a and b are RK equation of state parameters, and v is the molar volume. The α function is a temperature-dependent function, which has the following form proposed by Soave[6]

$$\alpha = [1 + m(1 - T_r^{0.5})]^2 \tag{5}$$

where T_r is the reduced temperature. The m parameter is correlated as a function of the acentric factor ω

$$m = 0.480 + 1.574\omega - 0.175\omega^2 \tag{6}$$

For any pure component, the values of a and b are calculated from the critical properties

$$a = 0.427471R^2T_c^{\,2}/P_c \tag{7}$$

$$b = 0.086641RT_c/P_c \tag{8}$$

where T_c and P_c are the critical temperature and pressure. For mixtures, the parameters in eq 4 can be calculated using the mixing rules

$$\alpha a = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j \alpha_{ij} a_{ij} \tag{9}$$

$$b = \sum_{i=1}^{N} x_i b_i \tag{10}$$

According to a quadratic mixing rule, the cross parameter α_{ij} is given by

$$\alpha_{ij}a_{ij} = (\alpha_i\alpha_j a_i a_j)^{0.5} \tag{11}$$

Equation 4 can be rearranged as

$$z^3 - z^2 + (A - B - B^2)z - AB = 0 \tag{12}$$

where z is the compressibility factor. A and B are defined as

$$A = \alpha a P/R^2T^2 \tag{13}$$

$$B = bP/RT \tag{14}$$

For a hydrogen-hydrocarbon system, Henry's constant is defined as

$$H = \lim_{x_1 \to 0} \frac{f_1^{\,L}}{x_1} = \lim_{x_1 \to 0} P\varphi_1^{L} \tag{15}$$

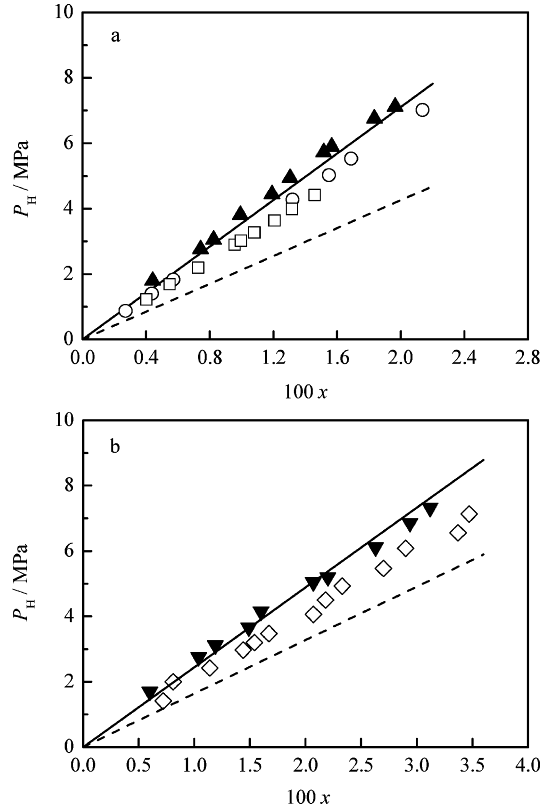

Figure 2. Comparison of experimental and predicted results of solubility of hydrogen in toluene: ▲, 298 K, this work; ▼, 343 K, this work; ○, 298 K, Brunner;[9] ◇, 343 K, Koschel et al.;[10] □, 303 K, Tsuji et al.[11] The solid line takes k_{ij} into account, while the dashed line does not.

where x_1, f_1^L, and φ_1^L are, respectively, the mole fraction, the fugacity, and the fugacity coefficient of hydrogen in the liquid phase. The fugacity coefficient can be derived from the SRK equation. Therefore, Henry's constant has the following expression

$$\ln H = \ln P_2 + \frac{B_1}{B_2}(z_2 - 1) - \ln(z_2 - B_2) + \frac{A_2}{B_2}\left[\frac{B_1}{B_2} - 2\left(\frac{A_1}{A_2}\right)^{0.5}(1 - k_{12})\right]\ln\left(1 + \frac{B_2}{z_2}\right) \quad (16)$$

where k_{12} is the binary interaction parameter between solute (hydrogen) and solvent (hydrocarbons). Gray et al.[7] correlated k_{12} with the critical temperature of solvent as follows

$$k_{12} = 0.0067 + 0.63375S^3/(1 + S^3) \quad (17)$$

$$S = (T_{c,2}/\mathrm{K} - 50)/(1000 - T_{c,2}/\mathrm{K}) \quad (18)$$

Equation 16 is applicable not only to pure hydrocarbons, but also to complex mixtures. The critical properties and other physical properties that are used in the present work, such as the vapor pressures of the pure solvents, are provided by Yaws.[8]

Results and Discussion

The hydrogen solubilities in pure hydrocarbons (benzene and toluene) are first measured. Figure 2 shows variations of the hydrogen solubilities in toluene with the hydrogen partial pressure P_H. P_H is calculated by subtracting the equilibrium pressure of solvent from the total pressure. As can be seen from the experimental results, the measured hydrogen solubilities are in good agreement with previous published data,[9,10] which justifies the experimental method used in this study. Moreover, a linear relationship is observed between P_H and x, which indicates that Henry's law is applicable within the temperature and pressure range studied. It seems that systematic positive derivations are obtained for the solubility of hydrogen in toluene in this work compared with those obtained by Brunner[9] and Koschel et al.[10] Actually, it is not the case. Tsuji et al.[11] recently reported experimental data for the hydrogen solubility in toluene, which are shown in Figure 2a. It can be seen that their results are almost the same as those obtained by Brunner,[9] although the two experiments are carried out at different temperatures, i.e., 298 K by Brunner and 303 K by Tsuji et al. On the other hand, our results are reliable compared with the data determined by Tsuji et al.[11]

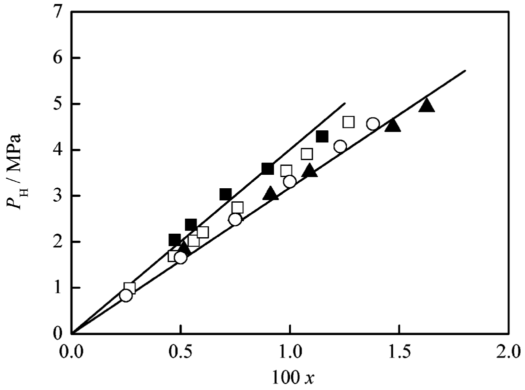

Figure 3. Solubility of hydrogen in benzene: ■, 298 K, this work; ▲, 323 K, this work; □, 303 K, Tsuji et al.;[11] ○, 323 K, Park et al.;[13] —, SRK prediction.

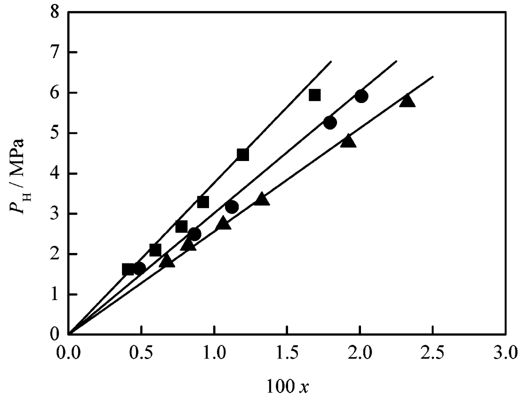

Figure 4. Solubility of hydrogen in BTXS: ■, 298 K; ●, 323 K; ▲, 343 K; —, SRK prediction.

The two lines shown in Figure 2 are the predicted results using the SRK equation. The solid line takes the binary interaction parameter into account, while the dashed line does not. It is obvious that the SRK equation considering the binary interaction parameters can successfully predict the hydrogen solubility in toluene, which is consistent with what Twu et al.[12] found. The following studies on other systems also validate this result.

The solubilities of hydrogen in benzene and BTXS are shown in Figures 3 and 4. The model output from the SRK equation is found to agree well with the experimental data. The hydrogen solubility measurements in benzene performed in this work agree with those obtained by linear extrapolation of the experimental data reported by Park et al.[13] to a lower hydrogen partial pressure, which again validates our experimental method. In addition, our experimental data for the hydrogen solubility in benzene are reliable in comparison with those obtained by Tsuji

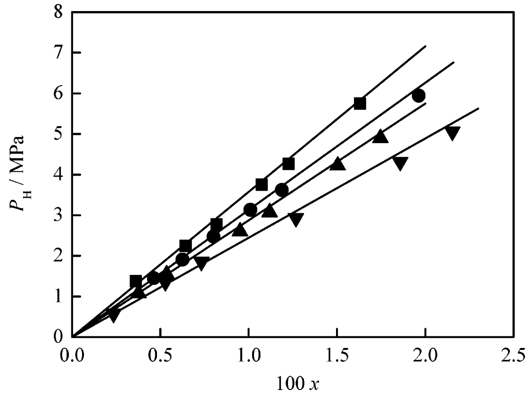

Figure 5. Solubility of hydrogen in pygas: ■, 298 K; ●, 313 K; ▲, 323 K; ▼, 343 K; —, SRK prediction.

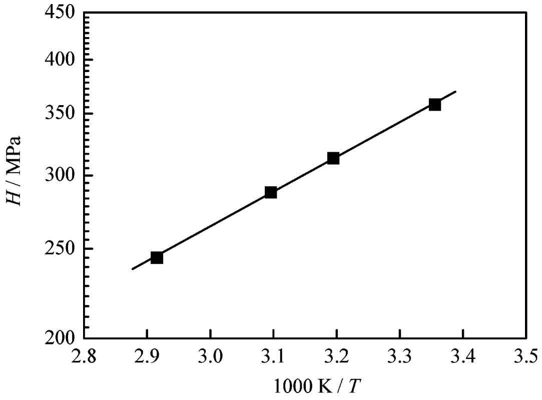

Figure 6. Effect of the temperature on Henry's constant for hydrogen in pygas system.

Table 3. Hydrogen Solubility in Pygas

298 K		313 K		323 K		343 K	
P_H/MPa	100 x	P_H/MPa	100 x	P_H/MPa	100 x	P_H/MPa	100 x
1.380	0.36	1.454	0.46	1.080	0.38	0.576	0.23
2.245	0.64	1.908	0.63	1.546	0.54	1.357	0.53
2.772	0.82	2.475	0.80	2.602	0.95	1.858	0.73
3.748	1.07	3.130	1.01	3.070	1.12	2.936	1.27
4.260	1.23	3.619	1.19	4.224	1.50	4.316	1.86
5.748	1.63	5.942	1.96	4.898	1.75	5.060	2.15

et al.[11] The Henry's constant, which is the slope of the solid line, decreases with increased temperature.

The hydrogen solubility measurements in pygas are shown in Table 3. As can be seen from the data, the hydrogen solubility in pygas increases with temperature and pressure. The same trend is followed for hydrogen in benzene, toluene, and BTXS.

Figure 5 compares the predicted results with the experimental measurements for the hydrogen solubility in pygas. Apparently, the model simulates the hydrogen solubility very well in the range of experimental conditions studied. The relative error between experimental data and predicted results is in the range from −5.6 % to +6.1 %, in both positive and negative directions.

The effect of temperature on Henry's constant for hydrogen in pygas is presented in Figure 6. It is shown that a linear relationship is satisfied between ln(H) and T. The temperature dependence of Henry's constant can be expressed as follows

$$\ln H = -\frac{\Delta S_S}{R} + \frac{\Delta H_S}{RT} \qquad (19)$$

where ΔH_S and ΔS_S are the molar enthalpy of solution and the molar entropy, respectively. The values for ΔH_S and ΔS_S can be deduced from Figure 6 and are equal to $\Delta H_S = 7.19 \pm 0.11$ kJ.mol^{-1} and $\Delta S_S = -139.63 \pm 0.33$ J.mol^{-1}.K^{-1}, respectively. In comparison with the results obtained by Ronze et al.,[3] it is shown that the solubilities of hydrogen in pygas and straight run gasoil are different, while the enthalpy of solution are close ($\Delta H_S = 7.93 \pm 0.01$ kJ.mol^{-1} determined by Ronze et al.).

Table 4. Henry's Constant for Hydrogen in Different Systems

T/K	H_{benzene}/MPa	H_{toluene}/MPa	H_{BTXS}/MPa	H_{pygas}/MPa
298	400.89	355.42	376.01	357.71
323	317.72	286.42	301.33	287.45
343	267.28	244.16	255.79	244.42

Henry's constant values for hydrogen in the four systems studied are listed in Table 4. It can be seen that the order of Henry's constant is $H_{\text{benzene}} > H_{\text{BTXS}} > H_{\text{pygas}} > H_{\text{toluene}}$, in contrast to the ranking based on the molecular weight. It seems that the hydrogen solubilities in monoaromatics monotonically increase with the molecular weights of the hydrocarbons.

This trend can be explained by a steric effect. The rise of the molecular weights of the monoaromatics means an increase in the number of side chains of the alkyl benzenes, which in turn leads to a widening of the intermolecular distance due to the effect of the alkyl group. It is conceivable that the widened distance or the large interspace is favorable for more hydrogen to dissolve into the monoaromatics. With benzene, toluene, and ethylbenzene as an example, the hydrogen solubilities in these monoaromatics conform to the order benzene < toluene < ethylbenzene, which is in agreement with the results previously reported by Fahim and Elkilani.[14] Inasmuch as BTXS and pygas are mainly composed of benzene and toluene, the hydrogen solubilities in these liquids are higher than those in benzene, but less than those in toluene. The lower solubility of hydrogen in BTXS compared with that in pygas may be caused by the alkane components in pygas, since the hydrogen solubilities in alkanes are higher than those in aromatics with the same number of carbons.[14]

Conclusions

In this work, the solubilities of hydrogen in four systems, i.e., benzene, toluene, benzene + toluene + xylene + styrene (BTXS), and pyrolysis gasoline (pygas) are individually measured on the basis of an isochoric method in an autoclave. The experimental method is validated with pure components, benzene and toluene. The Soave−Redlich−Kwong (SRK) cubic equation of state is used to predict the hydrogen solubility. It is found that the SRK equation taking account of the binary interaction parameter can predict Henry's constant very well. On the contrary, provided that the binary interaction parameter is equal to zero, the SRK equation will overestimate the hydrogen solubility.

The results show that the solubility of hydrogen in pygas increases with the rise of temperature and pressure, and Henry's law is applicable under the experimental conditions investigated. In addition, the steric hindrance of the alkyl group of the monoaromatics has a positive effect on hydrogen dissolution into the liquid. This effect results in the different solubilities of hydrogen in the above systems, viz., benzene < BTXS < pygas < toluene.

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