Hydrogen solubility in straight run gasoil

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Abstract

The solubility of hydrogen in a straight run gasoil is measured using a chromatographic method, which is first validated with a known organic liquid (cyclohexane). Under the experimental conditions (up to 4 MPa, temperatures from 298 to 675 K), these results are best described by Chao–Seader and improved Zudkevitch–Joffe (with adjustment parameter $b_0 = 0.6$) models. Henry's law constant is determined at four temperatures. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In many industrial processes of oil refining (hydrogenation, hydrotreatments such as hydrodesulfurization, hydrodenitrogenation, ...), kinetics is often related to the hydrogen pressure. However, in these processes the catalyst is in contact only with the liquid phase containing the dissolved hydrogen; therefore, the kinetic rate would involve the hydrogen concentration in the liquid phase. If mass transfers are not limiting (as expected in the Mahoney–Robinson reactor), hydrogen solubility in the conditions of reaction is a way to access a good estimation of the hydrogen concentration in the liquid phase; on the other hand, if a mass transfer limitation occurs, a diffusion model may be used, implying the knowledge of the liquid-phase hydrogen concentration. In both cases, the knowledge of hydrogen solubility is of interest for studying the kinetics of hydrotreatments.

Whereas many data are available for hydrogen solubility in pure components (Young, 1981), only few researchers have worked with complex mixtures, especially with petroleum products (Harrison, Scheppele, Sturm, & Grizzle, 1985). The aim of our work is to propose an experimental method to measure the solubility of hydrogen in a determined gasoil; the method is validated by measurements on cyclohexane (in which the hydrogen solubility has

been published). The experimental results obtained with gasoil will be compared to those calculated with various thermodynamic models.

2. Materials and methods

2.1. Materials

The apparatus (Fig. 1) used in this work was a high-pressure 300 cm^3 autoclave (Parr). A internal gas inducing impeller (at 900 rpm) was used to provide the mixing of the liquid phase (Blet et al., 1998); its hollow axis generated a good circulation of hydrogen between the upper gas space and the liquid-dispersed bubbles. A plunger tube allowed the liquid phase to be sampled (without pressure decrease) through a sampling valve (Siemens C79451) designed for high pressures and temperatures. The temperature in the valve was slightly lower than in the autoclave to avoid gas separation in the valve. The liquid sample (2.4 mm^3) was immediately vaporized and evacuated through a heated transfer line connected to a gas chromatograph with a thermal conductivity detector. Hydrogen analysis was performed on a 2 m length $-\frac{1}{8}''$ OD Porapak-Q^{TM} packed column (carrier [N_2] flowrate$=25$ cm^3 min^{-1}; oven temperature$=80°$C; detector temperature $= 120°$C); the TCD has tungsten wires for better sensitivity. The calibration curve of the detector was obtained from sampling pure hydrogen at room temperature and various pressures.

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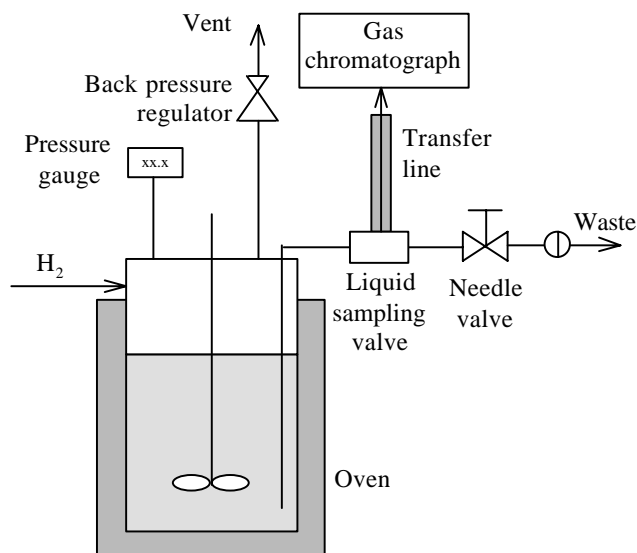*E-mail address:* dro@lgpc.cpe.fr (D. Ronze).

Fig. 1. Simplified scheme of the experimental system.

Cyclohexane (99.5%) was obtained from Aldrich Chemicals Co.

The main physical properties of the gasoil are:

specific gravity — $\rho = 863.6$ kg m^{-3} (293 K),
kinematic viscosity — $v = 8.0$ cSt $= 8.0 \times 10^{-6}$ m^2 s^{-1} (293 K),
refractive index — $n = 1.4795$,
carbon content — 86.2 wt%,
hydrogen content — 13.1 wt%,
sulfur content — 0.74 wt%.

The gasoil is represented by the distillation data (ASTM D86) given in Table 1.

2.2. Equilibrium pressure measurements

Equilibrium pressures of pure liquids (cyclohexane or gasoil) were first determined. The autoclave was filled with a known quantity of solvent (about 200 cm^3), and the permanent gases were evacuated under vacuum (3 kPa) for 2 h at room temperature; then the autoclave was isolated from the vacuum line and heated stepwise. The equilibrium pressure was determined from the total pressure at each constant temperature step.

2.3. Solubility measurements

The solubility measurements are carried out in the same autoclave, filled with about 200 cm^3 solvent. The autoclave

was then heated to the desired temperature and pressurized with hydrogen. Pressure within the cell was maintained by mean of a back-pressure regulator; when the desired pressure was reached, the hydrogen feed was stopped. Liquid samples were taken after the equilibrium was achieved (i.e. after maintaining constant pressure and temperature during $1\frac{1}{2}$ h); hydrogen was then admitted to compensate the small volume of liquid discharged and therefore to maintain the total pressure constant.

3. Modelisation

In order to compare our experimental results (equilibrium pressure and solubility measurements) to published models, we have simulated our system either with Hysys.Plant 2.1.1 software from Hyprotech®, using 15 distillation fractions as pseudo-components. Thermophysical properties of each pseudo-component are then calculated as a function of the operating conditions using published relations: specific gravity (Firoozabadi, 1988), specific heat, ideal enthalpy and vapor pressure (Lee & Kesler, 1975), molecular weight (Twu, 1984) and viscosity (Twu, 1985).

Five thermodynamic models are chosen among the most pertinent ones provided by the software. Two of them [Chao and Seader (1961), Jin, Greenkorn, and Chao (1995) and Grayson and Streed (1963)] are computing the vaporization equilibrium ratio K_i as

$$K_i = v_i^0 \frac{\gamma_i}{\phi_i}, \tag{1}$$

where the standard liquid fugacity coefficient v_i^0 is fitted with approximating functions within the framework of the principle of corresponding states, and the vapor fugacity coefficient ϕ_i is calculated from the Redlich and Kwong (1949) equation of state. The liquid solutions of hydrocarbons are considered to be regular solutions ($G^E = 0$); the activity coefficients γ_i are therefore determined using Hildebrand's equation (Hildebrand & Scott, 1950).

Due to the range of data used to fit the approximating functions, these models are restricted to pressures up to 25 MPa (Chao–Seader) or 55 MPa and temperatures up to 723 K (Chao–Seader) or 753 K (Grayson–Streed).

The remaining three models [Zudkevitch & Joffe, 1970; Peng, Robinson, Stryjec, Vera (PRSV) (Stryjek & Vera, 1986); Soave, 1972 recommended by API, 1992 Chap. 8] are based on a cubic equation of state, i.e.:

$$ZJ: \quad P = \frac{RT}{v - b} - \frac{a}{T^{1/2}v(v + b)}, \tag{2}$$

Table 1
Distillation data of the gasoil (atmospheric pressure)

Temperature (°C)	240	259	264.5	273	280.5	288.5	297.5	307.5	319.5	333.5	350.5	363.5	370.5
Cumulative percentage	0	5	10	20	30	40	50	60	70	80	90	95	100

$$PRSV: \quad P = \frac{RT}{v-b} - \frac{a}{v^2 + 2bv - b^2}, \tag{3}$$

$$API(cf.\ Soave, 1972): \quad P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)}. \tag{4}$$

Parameters a and b are calculated as functions of temperature and pressure according to the original publications.

For complex mixtures, the ZJ model has been improved in Hysys.Plant software by adjunction of a b_0 adjustment parameter, which applies to the b_i parameters (covolumes):

$$b_i = b_i^{ZJ} \left[1 + b_0 \left(\frac{T}{T_c} - 1 \right) \right]. \tag{5}$$

The original ZJ model is therefore obtained with $b_0 = 0$.

Only the improved ZJ model includes an adjustment parameter (b_0); parameters of other models are calculated without any reference or fitting to our experimental data.

4. Results and discussion

4.1. Cyclohexane measurements

The hydrogen solubility measurements in cyclohexane are shown in Table 2, where x_{H_2} is the hydrogen mole fraction in the liquid phase, which is calculated as

$$x_{H_2} = c_L \frac{M_L}{\rho_L}, \tag{6}$$

where c_L is the molar concentration of the solute in liquid phase (obtained from chromatographic analysis), M_L and ρ_L the molecular weight and the specific gravity of cyclohexane. The latter is calculated from relations of Thomson, Brobst, and Hankinson (1982) under experimental conditions.

Fig. 2 shows the comparison between these experimental data and the models, for each temperature.

In this case, Chao–Seader and Grayson–Streed correlations are almost undistinguishable, and are in relatively good agreement with our experimental results, as do the PRSV and API models.

Moreover, the apparent linear behavior of these curves suggests, as a simplifying assumption, that one could use Henry's law for dilute solutions, i.e.,

$$P_{H_2} = Hx_{H_2}, \tag{7}$$

where P_{H_2} is the partial pressure of hydrogen and x_{H_2} the mole fraction of hydrogen in the liquid phase.

The needed hydrogen partial pressure is deduced by subtracting the cyclohexane vapor pressure from the total pressure. Fig. 3a reports cyclohexane vapor pressure measurements, which are in good agreement with the Wagner equation (Wagner, 1973), completed by Reid, Prausnitz, and Poling (1987) for cyclohexane data.

The Henry's constant values are then deduced from Fig. 2 and reported in Fig. 3b and Table 3. These results are in good agreement with the published data (Fig. 3b), which validates our method for further experiments.

4.2. Gasoil experiments

The hydrogen solubility measurements in gasoil are shown in Table 4. Hydrogen mole fraction is determined from Eq. (6); according to Harrison et al. (1985), the small shift in molecular weight of a petroleum distillate residue — due to temperature variations — is expected to cause little change in gas solubility and thus can be neglected.

Fig. 4 shows the comparison between these experimental data and the models for each temperature. The corresponding standard deviations are given in Table 5.

Table 2
Hydrogen solubility in cyclohexane — experimental results

Temperature (K)	Total pressure (MPa)	Number of measurements	x_{H_2}	
			Mean value	Standard deviation[a]
304	0.131	30	0.00063	0.00007
	0.642	26	0.00291	0.00008
	2.68	27	0.01124	0.00014
	4.49	29	0.01887	0.00026
332	0.567	24	0.00290	0.00005
	2.40	28	0.01247	0.00020
	4.60	28	0.02345	0.00064
373	0.500	28	0.00261	0.00006
	2.69	23	0.01785	0.00054
	4.39	24	0.02951	0.00053

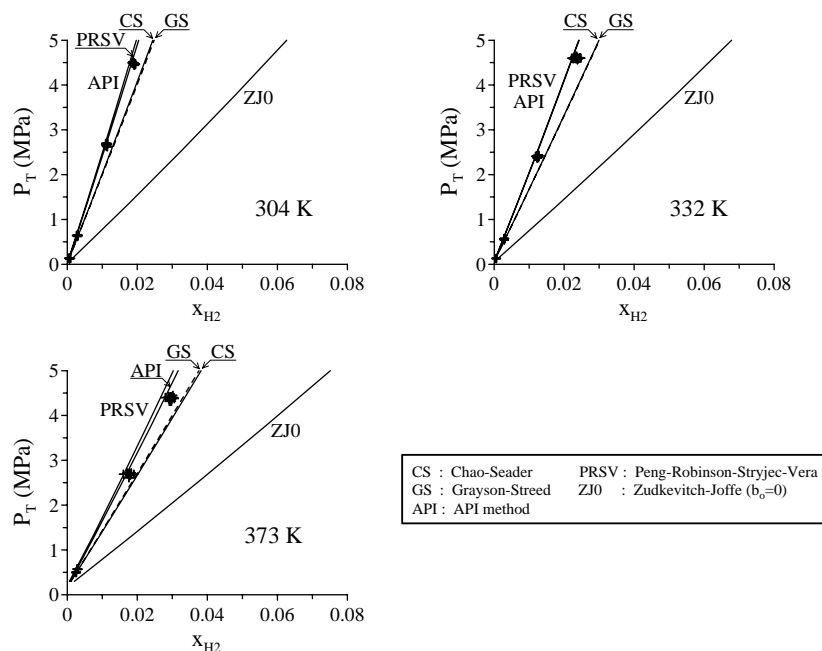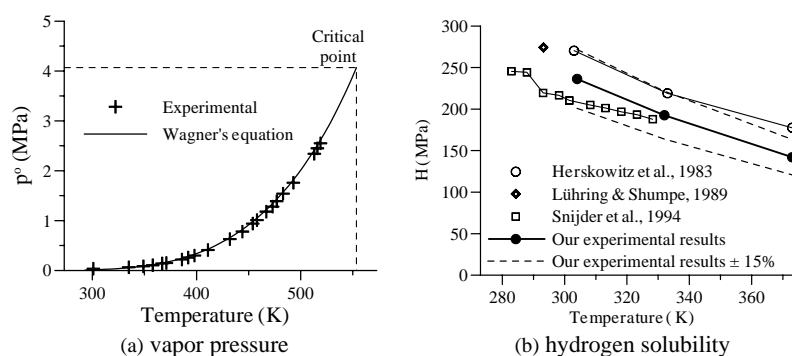[a]Standard deviation $= \sum_{i=1}^{n} \sqrt{(x_i - x_{mean})^2/(n-1)}$.

Fig. 2. Comparison of experiments and simulations (H_2/cyclohexane).

Fig. 3. Cyclohexane: (a) vapor pressure and (b) hydrogen solubility.

EoS models (PRSV, ZJ) are here far from the experimental data, except if the adjustment parameter b_0 (improved ZJ model) is set to 0.6

Among the tested correlations, Chao–Seader leads to the best description of the experimental results within the temperature and pressure range studied. Grayson–Streed and API correlations are also acceptable models, especially at lower temperatures.

In this pressure and temperature domain, the approximately linear behavior suggests the application of Henry's law, as in the cyclohexane case.

The needed hydrogen partial pressure is deduced by subtracting the equilibrium pressure from the total pressure. Fig. 5 reports gasoil equilibrium pressure measurements (Fig. 5a) and deduced Henry's constant values (Fig. 5b and Table 6). Equilibrium pressure measurements are in good agreement with the values obtained from the five investigated models.

Table 3
Hydrogen solubility in cyclohexane — Henry's law constant

Temperature (K)	304	332	373
H (MPa)	236	193	142

The Henry's law constant may be expressed as a function of temperature as follows:

$$\ln H = \frac{\Delta H_s}{RT}, \tag{8}$$

where ΔH_s is the molar heat of solution, constant within our experimental field.

From the plot in Fig. 6, we can deduce the value of $\Delta H_s = 7.93 \pm 0.01$ kJ mol^{-1}, which is in good agreement with the values calculated from Hysys.Plant$^{\circledR}$ results using Chao–Seader ($\Delta H_s = 7.32$ kJ mol^{-1}) or improved ZJ ($\Delta H_s = 7.93$ kJ mol^{-1}) models.

Table 4
Hydrogen solubility in gasoil — experimental results

Temperature (K)	Total (Mpa)	Number of measurements pressure	x_{H_2}		
			Mean value	Standard deviation	standard Cumulative deviation
298	0.220	30	0.00109	0.00018	0.0082
	0.937	38	0.00482	0.00026	
	1.37	55	0.00728	0.00059	
	1.81	41	0.00906	0.00071	
	2.44	40	0.01257	0.00076	
	3.18	52	0.01653	0.00153	
	3.92	42	0.02111	0.00104	
	5.32	31	0.03000	0.00212	
393	0.390	20	0.00468	0.00039	0.0194
	1.79	22	0.01684	0.00107	
	3.23	20	0.03554	0.00238	
	4.85	20	0.05546	0.00092	
	5.67	19	0.06414	0.00150	
524	0.967	28	0.01757	0.00196	0.0320
	2.26	29	0.04736	0.00161	
	3.32	29	0.06675	0.00289	
	4.39	30	0.09028	0.00164	
	5.57	23	0.11119	0.00161	
645	1.07	37	0.01444	0.00078	0.0318
	1.88	38	0.03996	0.00220	
	2.73	39	0.06920	0.00520	
	3.62	38	0.09880	0.00875	

CS = Chao Seader   PS = Peng-Robinson-Stryjec-Vera
GS = Grayson Streed   ZJ0 = Zudkevitch Joffe ($b_o = 0$)
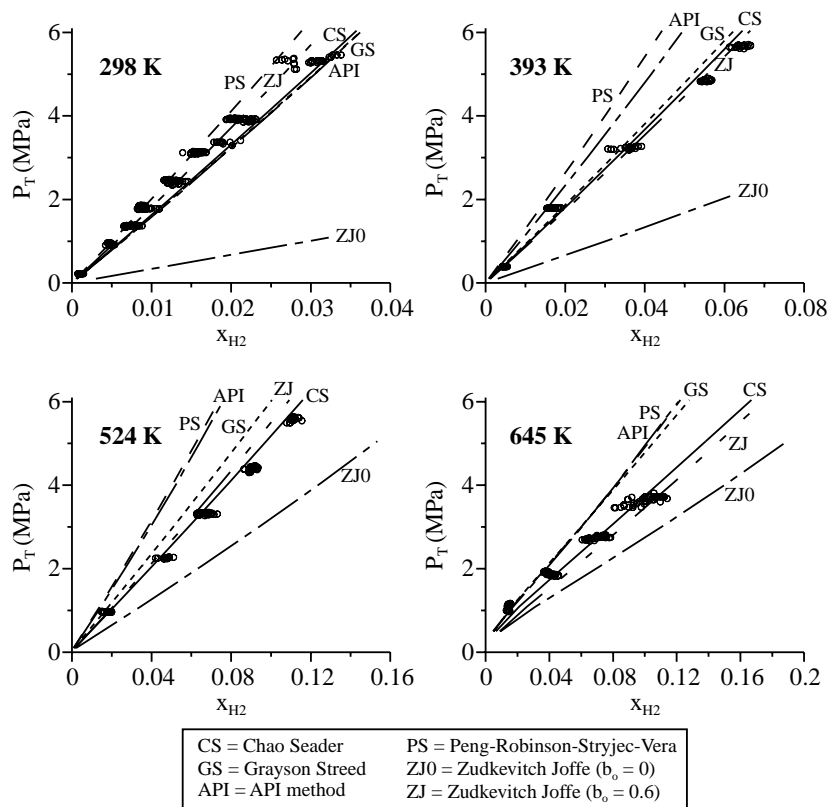API = API method   ZJ = Zudkevitch Joffe ($b_o = 0.6$)

Fig. 4. Comparison of experiments and simulations (H_2/gasoil).

Table 5
Standard deviations[a] between experimental and calculated H_2 mole fraction

Temperature	298 (K)	393 (K)	524 (K)	645 (K)	Cumulative
Experimental	0.0082	0.0194	0.0320	0.0320	0.0222
Chao–Seader	0.0024	0.0028	0.0039	0.0059	0.0037
Zudkevitch–Joffe ($b_0 = 0.6$)	0.0012	0.0024	0.0071	0.0104	0.0058
Grayson–Streed	0.0027	0.0037	0.0127	0.0156	0.0093
API	0.0025	0.0108	0.0266	0.0156	0.0143
Peng–Robinson–Stryjec–Vera	0.0016	0.0141	0.0280	0.0158	0.0152
Zudkevitch–Joffe ($b_0 = 0$)	0.0674	0.0639	0.0374	0.0283	0.0553

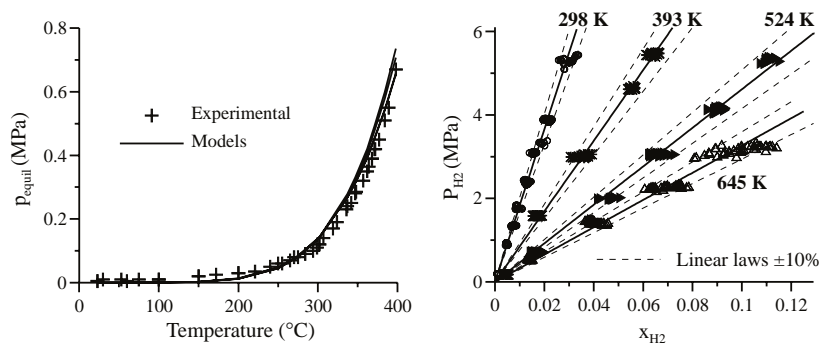[a]Model standard deviation $= \sum_{i=1}^{n} \sqrt{[(x_i - x_{\mathrm{mod}})^2]/(n-1)}$.

Fig. 5. Gasoil: (a) equilibrium pressure and (b) hydrogen solubility.

Table 6
Hydrogen solubility in gasoil — Henry's law constant

Temperature ($^{\circ}$C)	298	393	254	645
H (MPa)	183	84.6	46.2	32.7

5. Conclusion

A chromatographic method is used for hydrogen solubility measurements in gasoil, in order to determine the hydrogen concentration in the liquid phase. The method is first validated with cyclohexane published data, then run to determine the hydrogen solubility in gasoil under pressures up to 4 MPa and temperatures up to 645 K. The Chao–Seader and Z-J (with $b_0 = 0.60$) models can be used to describe the hydrogen solubility in the gasoil, thereby allowing the calculation of the hydrogen liquid concentration during a catalytic test run. The relationship between hydrogen partial pressure and liquid-phase composition appears to be linear (Henry's law) in our experimental range; Henry's constant varies from 183 MPa (at 298 K) to 32 MPa (at 645 K).

Fig. 6. Effect of temperature on Henry's constant.

Notation

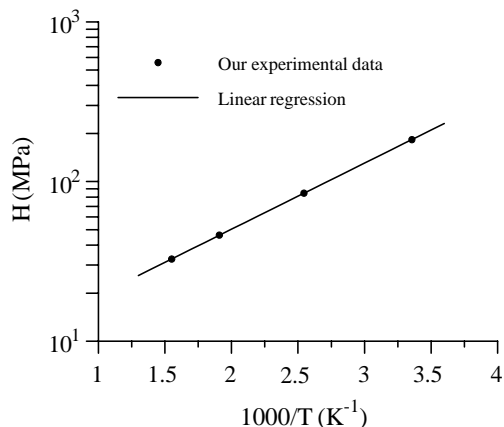|	
a	EoS parameter, dimension according to Eqs. (2)–(4)
b	Redlich–Kwong covolume, m^3 mol^{-1}
b_0	adjustment parameter (improved ZJ model), dimensionless
b_i	Redlich–Kwong covolume (improved ZJ model), m^3 mol^{-1}
b_i^{ZJ}	Redlich–Kwong covolume (ZJ model), m^3 mol^{-1}
c_L	concentration of the solute in the liquid phase, mol m^{-3}
H	Henry's law constant, MPa
M_L	molecular weight of the liquid phase, kg mol^{-1}

n	refractive index, dimensionless
P	pressure, MPa
R	gas law constant, J mol^{-1} K^{-1}
T	temperature, K
T_c	critical temperature, K
v	molar volume, m^3 mol^{-1}
x	molar fraction, dimensionless

Greek letters

ΔH_s	molar heat of solution, kJ mol^{-1}
v	kinematic viscosity, m^{2}s^{-1}
ρ	specific gravity, kg m^{-3}

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