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Solubility of hydrogen in methanol at temperatures from 248.41 to 308.20 K

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Abstract

Isothermal hydrogen solubility in methanol has been measured at six temperatures: 248.41, 263.38, 278.01, 278.25, 291.20 and 308.20 K up to 3.4 MPa. Hydrogen solubility has been found an increasing function of temperature in the range of studied temperatures. The apparatus used in this work can be operated either as a static–analytic technique with a "on line" gas chromatograph or as a synthetic one. The static–analytic method takes advantage of a movable pneumatic capillary sampler (Rolsi^{TM}, Armines' patent). The apparatus was used following a synthetic mode at 278.25 K from 0.04 to 0.33 MPa in order to compare the data obtained through the two techniques. The data are congruent. A comparison analysis is performed with measurements from Bezanehtak et al. [K. Bezanehtak, G.B. Combes, F. Dehghani, N.R. Foster, J. Chem. Eng. Data, 47 (2002) 161–168], Wainwright et al. [M.S. Wainwright, T. Ahn, D.L. Trimm, N.W. Cant, J. Chem. Eng. Data, 32 (1987) 22–24], Yorizane et al. [M. Yorizane, S. Sadamoto, H. Masuoka, Y. Eto, Kogyo Kagaku Zasshi, 72 (1969) 2174–2177] and Liu et al. [Q. Liu, F. Takemura, A. Yabe, J. Chem. Eng. Data, 41 (1996) 1141–1143]. The Henry's law constants were calculated, and a temperature dependent empirical correlation has been produced, based on experimental data.

Keywords: Solubility data; Hydrogen; Methanol; Henry's law; Low temperature; Modeling

1. Introduction

Solubility data of gases in liquid are fundamental properties for the study of gas absorption and desorption in gas separation processes. The solubility of hydrogen in methanol is an important property for the estimation of hydrogen losses by co absorption from a synthesis gas. This question is more accurate for CO_2 capture, the hydrogen is the most important compound for the hydrogen fuel gas (in the combustion turbine for Integrated Gasification Combined Cycle (IGCC) plants) and its concentration is very high. This is the case for CO_2 separation by physical absorption using methanol as solvent. Vapor–liquid equilibrium data for the hydrogen–methanol binary systems have been published recently from 278 to 323 K and from 0.5 to 5 MPa [1–5], and at higher pressure by Brunner et al. [6], from 5 until 100 MPa (Table 1). A few experimental measurements were published for temperature lower than 278 K, Yorizane et al. [7], Katayama and Nitta [8] at atmospheric pressure for five temperatures (Table 1), Takeuchi et al. [9] at 5 MPa and for two temperatures. However, solubility data of the hydrogen–methanol binary systems display a high degree of inconsistency as it can be seen for example Fig. 1, for the data measured in the 291–298 K range. That is why we measured the hydrogen solubility data in methanol with two different experimental methods at five temperatures, from 248 to 308 K, and from 0.43 up to 3.4 MPa in order to understand the reason of these inconsistencies in bubble curves, performing a comparison with literature data.

It is always difficult to measure data for systems containing methanol due to water content. Bezanehtak et al. [1] chose a static–analytic technique with liquid phase recirculation and

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Nomenclature

f	fugacity (MPa)
H	Henry's law constant (MPa)
n	mole number (mol)
P	pressure (MPa)
$\bar{P}$	partial pressure (MPa)
R	gas constant ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
S.D.	standard deviation
T	temperature (K)
υ	molar volume ($\mathrm{kmol\,m^{-3}}$)
V	volume ($\mathrm{m^3}$)
x	liquid mole fraction

Greek letters

α	non-randomness NRTL parameter
ϕ	fugacity coefficient
τ	NRTL model binary interaction parameter ($\mathrm{J\,mol^{-1}}$)

Subscripts and superscripts

gas	gas phase
i	species i
liquid	liquid phase
s	saturated state
1	methanol
2	hydrogen
∞	infinite dilution state

on line gas chromatography. Samplings are achieved through rotating sampling valves.

Sampling valve for liquids is in the recirculation line with the problem of introducing carrier gas from the loop when moving back the valve. Sampling valve for vapor is at the end of tubing implying an important purge with special care not to create a drastic pressure drop and then to hope getting reliable samples. Wainwright et al. [2] used the same technique as Yorizane et al. [7], unfortunately the paper from Yorizane et al. is written in Japanese and then difficult to discuss. Choudary et al. [3] and Radhakrishnan et al. [4] use a different technique, they saturate methanol with hydrogen inside an autoclave at desired T and P. After equilibration they transfer to a gas burette a given amount of liquid phase with the risk of a non-negligible pressure decrease (modification of the equilibrium inside the equilibrium cell) and finally they measure the volume of desorbed hydrogen at atmospheric pressure. A synthetic method with total pressure measurement was chosen by Liu et al. [5]. The quantities of absorbed H_2 are determined from the pressure drop in the equilibrium cell observed between the pressure at end of loading and the pressure at equilibrium after stirring.

Table 1
Published data for hydrogen–methanol binary system

Reference	T (K)	P (MPa)
Bezanehtak et al. [1]	278, 288, 298, 308	2–11
Wainwright et al. [2]	291	1.1–4.85
Choudary et al. [3]	293, 308, 318, 328	0.44–2.1
Liu et al. [5]	296–323	0.5, 1 and 1.5
Brunner et al. [6]	298, 323, 373	5–100
Yorizane et al. [7]	243, 258, 291	1–5
Katayama and Nitta [8]	213, 233, 253, 273, 298	0.1
Takeuchi et al. [9]	223, 273	5

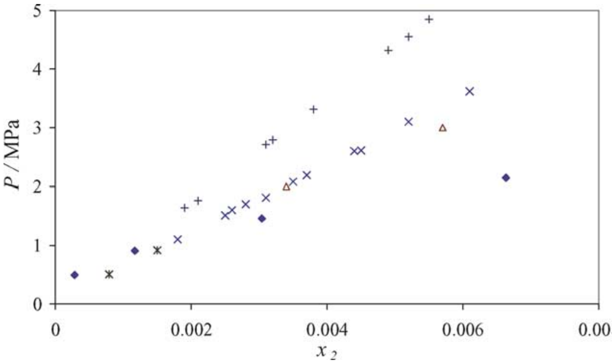

Fig. 1. Solubility data of hydrogen in methanol. (△) 298 K from Bezanehtak et al. [1]; (+) 291 K from Wainwright et al. [2] (synthetic method); (×) 291 K from Wainwright et al [2] (static–analytic); (♦) 293 K from Choudary et al. [3]; (✱) 296 K from Liu et al. [5].

The problem is during loading the hydrogen begins to dissolve and consequently the quantity determined in this way will be underestimated. Katayama and Nitta [8] used a static method with mercury displacement that allows measurements of solvent and vapor phase volumes. This technique looks like the previous one but here the determination of dissolved hydrogen comes from the pressure difference observed in the filling reservoir, which is more satisfactory. As can be analyzed the same techniques were used by authors with very different results (Fig. 1). In this work, a static–analytic technique was chosen to achieve five isotherms measurements and a synthetic method for one isotherm at 278.25 K and from 0.04 to 0.33 MPa in order to confirm the "static–analytic" measurements. The experimental technique is based on a static analytic method using an on line gas chromatography, using a movable pneumatic capillary samplers (Rolsi$^{\mathrm{TM}}$, Armines' patent), allowing precise sampling of the liquid phase, and particular attention were taken into account for the synthetic method in order to have accurate measurements of gas and liquid volume.

2. Experimental section

2.1. Materials

Hydrogen is from L'Air Liquide, its certified purity is higher than 99.999%. The methanol was purchased from Prolabo with purity higher than 99.8%. Methanol was degassed

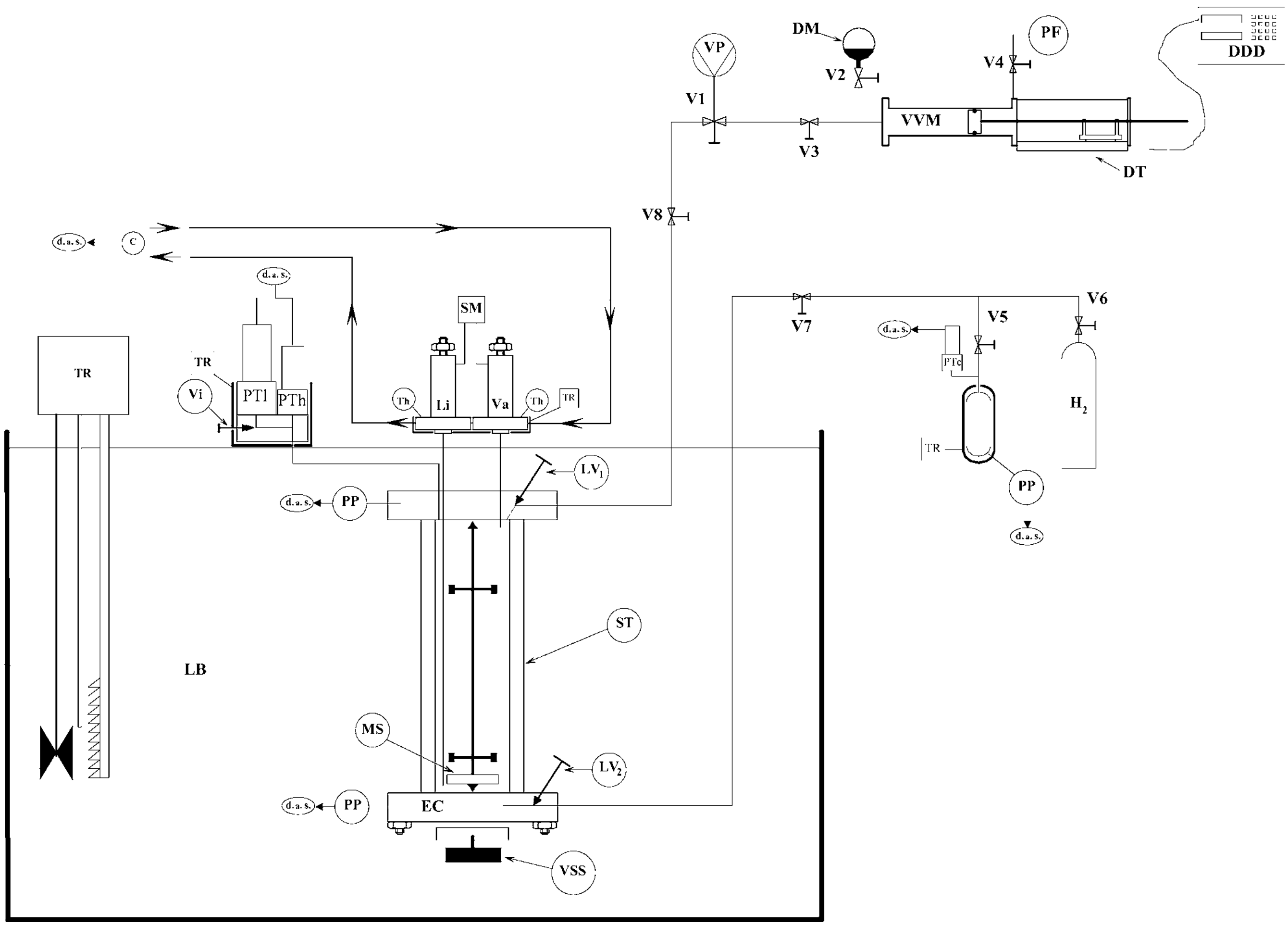

Fig. 2. C, carrier gas to chromatograph; Da, data acquisition unit; DDD, displacement digital display; DM, degassed methanol; DT, displacement transducer; LB, liquid bath; PF, pressurising fluid; PP, platinum probe; PT, pressure transducer; SM, sampler monitoring; ST, sapphire tube; Th, thermocouple; V, shut-off valve; V_1 and V_2, feeding valves; VP, vacuum pump; VSS, variable speed stirring; VVC, variable volume cylinder.

under a vacuum prior to any experiment in order to avoid the presence of non-condensable species.

2.2. Apparatus and experimental procedures

Measurements have been performed using the apparatus described in Fig. 2. This apparatus is partly similar to the apparatus described by Laugier and Richon [10] especially for the static analytic part. The equilibrium cell (30 cm^3 volume) is composed of a sapphire tube pressed between two Hastelloy pieces. The bottom flange holds a magnetic stirring assembly. The equilibrium cell was immersed in a thermoregulated liquid bath. Two platinum resistance thermometers (Pt 100 Ω) inserted inside wells drilled in both flanges of the equilibrium cell at the top and the bottom of the cell are connected to an HP data acquisition unit (HP34970A). These two platinum resistance thermometers are periodically calibrated against a 25 Ω reference platinum resistance thermometer (Tinsley Precision Instruments). The uncertainty is less than 0.02 K. The 25 Ω reference platinum resistance thermometer was calibrated by the Laboratoire National d'Essais (Paris) based on the 1990 International Temperature Scale (ITS 90). Pressures are measured by means of two pressure transducers (Druck, PTX611 model, range from 0 to 0.25 MPa for low pressures and from 0 to 2.5 MPa for higher pressure) connected to the HP data acquisition unit. The pressure transducers are maintained at constant temperature (higher than the highest temperature of the study). The pressure uncertainty is estimated to be ±0.001 MPa for the 2.5 MPa pressure transducer, and ±40 Pa for the 0.25 MPa pressure transducer. The analytical measurements were carried out with a gas chromatograph (VARIAN) fitted with a thermal conductivity detector. Peak integrations were performed with a commercial software (BORWIN, from JMBS, Le Fontanil, France). The analytical column used is Porapak R maintained at 393 K. The TCD was calibrated by introducing known amounts of pure compounds through adequate syringes directly inside the gas chromatograph injector. The accuracy of liquid mole fraction analyses is estimated to be ±4% over the whole range of concentrations.

Methanol was stored in a volumetric pump, which allowed controlled injections of the compounds into the equilibrium cell. The pump consists in a variable volume cylinder connected to an opto-electronic displacement transducer and a pressurizing circuit (helium). Hydrogen was injected in the equilibrium cell from a constant volume vessel (56 cm^3) maintained at a pressure higher than the cell pressure. The hydrogen vessel has its own calibrated (similar procedure as for equilibrium cell probes) pressure transducer and platinum resistance thermometer. The volumes of the hydrogen vessel and of the equilibrium cell were accurately measured (56.36 ± 0.04 and 33.64 ± 0.04 cm^3, respectively).

2.3. Methods

The experimental procedure for the static–analytic method consists first in evacuating the cell and the loading lines. The cell is then thermostated at the desired temperature in the liquid bath. The degassed methanol is introduced into the equilibrium cell from the variable volume cell, through evacuated loading line, and a small amount of hydrogen is loaded just after recording the initial temperature and the corresponding vapor pressure of methanol. The system is stirred until the equilibrium is reached. At least 10 samples are withdrawn using the pneumatic samplers ROLSI^{TM} as described by Guilbot et al. [11] and analyzed by the gas chromatograph in order to check for measurement repeatability. More Hydrogen is then introduced into the cell through successive loadings followed by samplings and analyses to determine the isothermal bubble curves.

The experimental procedure for the synthetic method consists in the introduction of known amount of degassed methanol in the thermostated equilibrium cell. The displacement of the piston (contained in the variable volume cylinder) and the pressure and temperature of the variable volume cylinder are recorded. After measurement of the vapor pressure, hydrogen is introduced from the storage vessel, the pressure and temperature of which is recorded before and after each loading. The HP on line data acquisition unit is connected to a computer to allow real time readings and storage of both pressure and temperature data. Efficient stirring helps the equilibrium to be reached. After about 10 min the pressure becomes stable indicating the equilibrium is reached, and then stirring is stopped. The complete run to determine the isothermal data with this method began with the measurement of pure solvent vapor pressure, and then vapor pressures after successive injection of hydrogen until 0.4 MPa was reached in the cell. From the known quantities of substances injected into the equilibrium cell the total compositions can be determined. Gas volume was minimized during methanol loading, and measurements were performed for low pressure value in order to reduce the uncertainty due to approximations made in the calculation. The numbers of moles of hydrogen introduced into the cell vapor phase are calculated by the ideal gas relationship (Eq. (4)).

$$n_2^{\text{gas}} = \frac{\bar{P}_2 V}{RT} \tag{1}$$

where $\bar{P}_2$ is the hydrogen partial pressure obtained by subtracting the methanol vapor pressure to the total pressure, V the volume of gas, i.e. the difference between the total cell volume and the volume filled by liquid methanol, R the gas constant (8.31 J mol^{-1} K^{-1}) and T the absolute temperature. The hydrogen number of moles dissolved in the liquid phase, n_2^{liquid}, is the difference between the loaded number of moles in the cell n_2 and the number of moles, n_2^{gas}, remaining in the vapor phase. The mole fraction of dissolved gas in methanol and the Henry's law constant are given by Eqs. (3) and (4):

$$n_2^{\text{liquid}} = n_2 - n_2^{\text{gas}} \tag{2}$$

$$x_2 = \frac{n_2^{\text{liquid}}}{n_1^{\text{liquid}} + n_2^{\text{liquid}}} \tag{3}$$

$$H_2^{\infty}(T, P) = \lim_{x_2 \to 0} \frac{f_2^{\text{liquid}}}{x_2} = \frac{\bar{P}_2}{x_2} \tag{4}$$

The methanol volume loaded in the cell was measured by the displacement sensor. The methanol number of moles n_1 loaded is then calculated using the molar volume of methanol v_1 (kmol m^{-3}), calculated using Eq. (5). This equation is based on [12]

$$v_1 = \frac{A}{B^{(1+(1-T/C)^D)}} \tag{5}$$

which is valid for temperatures from 175.47 to 512.64 K with $A = 2.288$ kmol m^{-3}, $B = 0.2685$, $C = 512.64$ K, $D = 0.2453$, and T (K), where the four parameters are from Component Plus^{TM} database (part of the simulation, optimization and calculation software from Prosim SA, version 3.1, 2002).

3. Results and discussion

Table 2 gives the solubility of hydrogen in methanol in the (248–308 K) range, measured through the static–analytic method. Uncertainties on temperatures and pressures are ±0.02 K and ±0.001 MPa, respectively. Uncertainties on hydrogen mole fractions are estimated to within ±8% as a result of calibration and measurement repeatability. The hydrogen solubility in methanol is an increasing function of temperature over the range of studied conditions. The hydrogen solubility in methanol follows the Henry's law in the studied range. The Henry's law constant has been calculated from the measured data and the measured saturated vapor pressure of methanol, with Eq. (4). The value is 705 ± 30 MPa at 278.01 K for the static–analytic method. Table 3 gives the mole fractions and the Henry's law constants obtained with the synthetic method at 278.25 K. The Henry's law constant calculated from the measured data obtained with the synthetic method at 0.0786, 0.14325, 0.1999 and 0.3327 MPa is equal to 730 ± 20 MPa. The Fig. 3 presents the solubility data measured with the two experimental techniques displaying a very good agreement. The

Table 2
Solubility of hydrogen in methanol measured using the static–analytic method, and the corresponding standard deviation due to repeatability

T (K)	P (MPa)	x_2	S.D. x_2
248.41	0.0006	0	
	0.561	0.00057	0.00001
	1.361	0.00148	0.00004
	2.271	0.00241	0.00004
263.38	0.0021	0	
	0.4820	0.00058	0.00001
	0.967	0.00108	0.00002
	1.550	0.00184	0.00003
	2.040	0.00235	0.00007
	3.026	0.00340	0.0002
278.01	0.0062	0	
	0.4533	0.00062	0.00003
	0.603	0.00082	0.00002
	0.920	0.00124	0.00001
	1.319	0.00188	0.00001
	1.558	0.00213	0.00002
	1.984	0.00284	0.00003
	2.564	0.00347	0.00008
	3.011	0.00413	0.00009
291.20	0.0117	0	
	0.4327	0.00070	0.00005
	1.292	0.00196	0.00001
	3.104	0.00477	0.00007
	2.514	0.00375	0.0001
308.20	0.0277	0	
	0.752	0.00134	0.00002
	1.383	0.00260	0.00009
	2.635	0.00484	0.0001
	3.427	0.00619	0.00003

Table 3
Solubility of hydrogen in methanol and Henry's law constant at 278.25 K, measured using the synthetic method

P (MPa)	x_2	H (MPa)
0.0404	0.000042	820
0.0786	0.000097	740
0.14325	0.000185	740
0.1999	0.000268	720
0.3327	0.000447	730

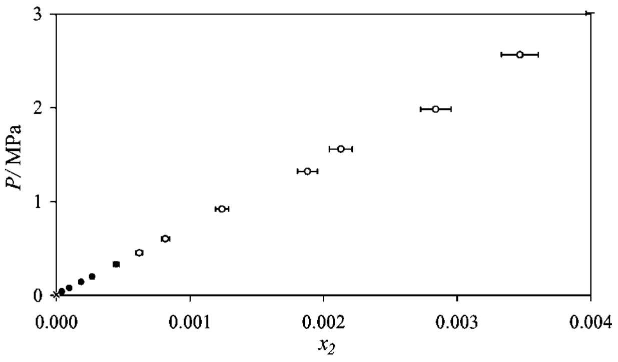

Fig. 3. Solubility of hydrogen in methanol at 278.25 K measured with the two methods: (○) static–analytic method and (●) synthetic method.

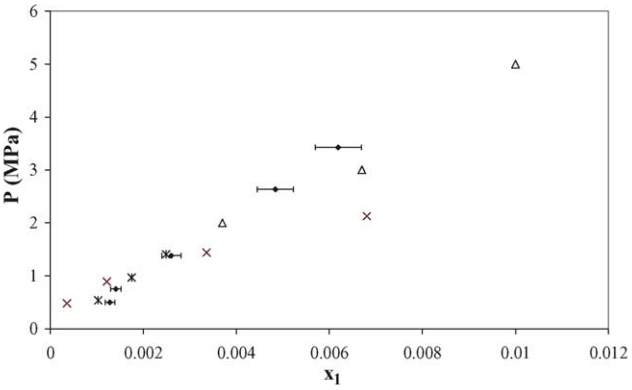

Fig. 4. Solubility data of hydrogen in methanol. (△) 308.15 K, Bezanehtak et al. [1]; (×) 308 K, Choudary et al. [3]; (✱) 313 K, Liu et al. [5]; (●) this work at 308.3 K.

Henry's law constant calculated value is close to the values measured by Liu et al. [5], from the correlation given in this reference we find: 660 ± 66 MPa at 278.25 K. The comparisons of our data with published data in the (308–313 K) temperature range (Fig. 4) allows us to point out some inconsistencies between the authors as described below.

4. Data comparisons

Gas solubility is controlled by phase equilibrium equations. Thus, for any component i, the liquid and the gas phase fugacities are equal, i.e.

$$f_i^{\text{gas}} = f_i^{\text{liquid}} \tag{6}$$

The Henry's law is used to determine the solute (hydrogen) fugacity. It assumes that

$$\Phi_i y_i P = H_{i,\text{solvent}} x_i \tag{7}$$

Here, the value of the hydrogen fugacity coefficient, Φ_i, calculated through the Peng–Robinson Equation of State (PR EoS) [13] is close to one (for example at 373.15 K and 2 MPa, $\Phi_i = 1.007$). As a consequence, the vapor phase can be considered as an ideal gas, and then Eq. (7) can be replaced by Eq. (8):

$$y_i P = H_{i,\text{solvent}} x_i \tag{8}$$

Henry's law constant is pressure dependent as expressed by Eq. (9):

$$\ln\left(\frac{\bar{P}_i}{x_i}\right) = \ln\left(H_{i,\text{solvent}}^{P^{\text{s}}_{\text{solvent}}}\right) + \frac{v_i^{\infty}}{RT}\left(P - P^{\text{s}}_{\text{solvent}}\right) \tag{9}$$

with v_i^{∞} the solute partial volume in liquid phase at infinite dilution and $H_{i,\text{solvent}}^{P^{\text{s}}_{\text{solvent}}}$ the Henry's constant at saturation pressure of the solvent, $P^{\text{s}}_{\text{solvent}}$. On Fig. 5 appears $\ln(\bar{P}_2/x_2)$ versus P corresponding to Bezanehtak et al. [1], Wainwright et al. [2], Yorizane et al. [7] and Liu et al. [5] data. From the trend of $\ln(\bar{P}_2/x_2)$ versus P at different temperatures we

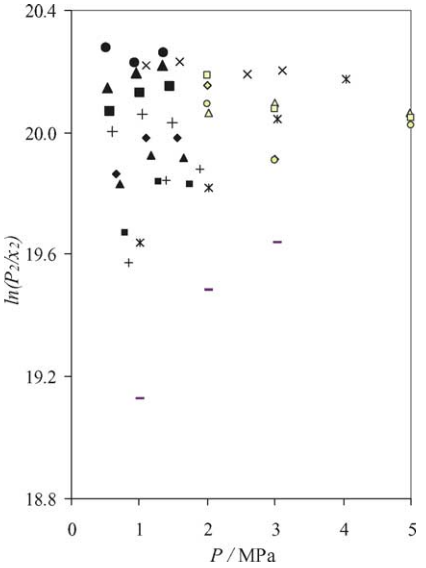

Fig. 5. Solubility of hydrogen at low pressures: (×) 291 K, Wainwright et al [2]; (●) 297 K, (▲) 303 K, (■) 313 K, (+) 323 K, (♦) 333 K, (▲) 343 K, (■) 353 K, (+) 373 K, Liu et al. [5]; (△) 278 K, (□) 288 K, (◇) 298 K, (○) 308 K, Bezanehtak et al. [1]; (-) 258.15 K, (✱) 291 K, Yorizane et al. [7].

can say the data produced by Bezanehtak et al. seem to be quite suspect. Indeed, $\ln(\bar{P}_2/x_2)$ obtained with these authors' data at 278, 288, 298 and 308 K is not a linear function of pressure. This is in full disagreement with what is observed from Liu et al. or Wainwright et al., then Yorizane et al. data can be considered as also quite suspect. Choudary et al. data are not considered in this study, as their $\ln(\bar{P}_2/x_2)$ values are much smaller than what is observed from other authors, for this reason $\ln(\bar{P}_2/x_2)$ versus P from Choudary et al. is not presented in Fig. 5.

Brunner et al. [6] have done measurements on this system at high pressures, at 298.15, 323.15 and 373.15 K. These data are interesting as a basis for a comparison as they were performed in both liquid and gas phases. These data were extrapolated to low pressures using a correlation based on a symmetric approach (Φ–Φ). The Peng–Robinson Equation of State was chosen with the Twu et al. [14] alpha function and the Huron–Vidal mixing rules [15] involving the NRTL activity coefficient model [16] ($\alpha_{i,j} = 0.3$). The objective function F_{obj} is relative to the calculated and experimental pressures and vapor compositions. The NRTL parameters are presented in Table 4. The mean average deviation on pressure is around 1%. The calculated hydrogen partial volume at infinite dilution in liquid phase is very low ($\cong 0.92 \times 10^{-5}$ m^3 mol^{-1}). $\ln(\bar{P}_2/x_2)$ versus P curves, Fig. 6, calculated through (Eq. (9)) with infinite dilution partial molar volume from Brunner show a good agreement between Brunner's and our's data. Slopes of $\ln(\bar{P}_2/x_2)$ versus P curves observed from Figs. 5 and 6 confirm data of Liu are very suspicious.

Table 4
NRTL parameters for the hydrogen (2)–methanol (1) system and objective function (on pressure) values obtained on data from Brunner et al. [6]

T (K)	τ_{12} (J mol^{-1})	τ_{21} (J mol^{-1})	S.D. τ_{12}	S.D. τ_{21}
298.15	8812	−187	126	14
323.15	7342	−138	126	14
373.15	8377	−286	1812	212

S.D., standard deviation.

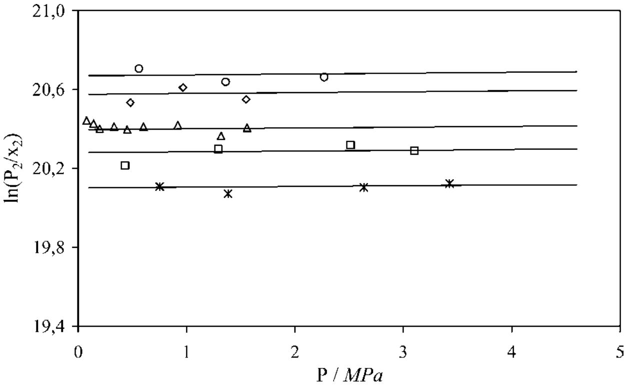

Fig. 6. Solubility of hydrogen at low pressure: (○) 248.41 K, (◇) 263.38 K, (△) 278.01 K, (□) 291.20 K, (✱) 308.20 K, this work; solid lines are predictions with a model extrapolated from Brunner et al. [6].

By definition, the Henry's coefficient can be obtained considering Eq. (9) at the solvent saturated pressure (at constant temperature) with the infinite dilution volume determined previously. An empirical correlation is determined (Eq. (10)) for H_2 in methanol. The uncertainty is close to ±10%.

$$H_{2,\text{solvent}} = \exp\left(19.7009 + \frac{1.7327}{T} + 0.6885\ \ln(T) - 0.01160T\right) \tag{10}$$

5. Conclusions

Isothermal hydrogen solubility data in methanol have been measured. A static–analytic technique with on line gas chromatography has been used for the five isotherms 248.41, 263.38, 278.01, 291.20 and 308.20 K. A synthetic method has been used at 278.25 K from 0.04 to 0.33 MPa to obtain data that have been found congruent with the data measured with the static–analytic technique. Our data have been compared to data from literature.

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