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Solubility of Hydrogen in Methanol, Nitrobenzene, and Their Mixtures. Experimental Data and Correlation[†]

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The solubility of hydrogen in nitrobenzene and methanol was studied in a temperature range of 25–70 °C and at hydrogen partial pressure up to 60 atm (6060 kPa). The solubility was also determined in mixtures of nitrobenzene and methanol at various concentrations. The values of the heat of solution of hydrogen in methanol and nitrobenzene were found to be 3.725 and 3.810 kJ/mol, respectively. A method to correlate the solubility data based on thermodynamic parameters has been described for both single solvent and mixtures. The effect of temperature as well as the heat of solution can also be predicted with this method.

Introduction

A knowledge of solubility of gases in liquids is necessary in the interpretation of the kinetics of gas–liquid and gas–liquid–solid reactions. This paper concerns experimental determination of the solubility of hydrogen in methanol, nitrobenzene, and their mixtures. Such data are required, for instance, to analyze the results of slurry hydrogenation of nitrobenzene (*1*) using methanol as a solvent. The solubility of hydrogen in methanol has been reported by Stephen and Stephen (*2*) for pressures of 1.01×10^2–5.878×10^4 kPa and temperatures of 25–140 °C. The solubility of hydrogen in nitrobenzene has been reported by Gjaldbaek (*3*) at 25 °C and atmospheric pressure. However, a systematic study of the solubility of hydrogen in nitrobenzene has not yet been published. Also, no data have been published for the solubility of hydrogen in mixtures of methanol and nitrobenzene at higher temperatures and pressures. This paper presents the solubility data for hydrogen in mixtures of methanol and nitrobenzene as well as in pure solvents at different temperatures and partial pressures of hydrogen. A method has been described to correlate the solubility data.

Experimental Method and Procedure

The technique used in this work for determination of the solubility of hydrogen under pressure involves measurement of desorbed hydrogen from the sample. In this method the solvent is first saturated with hydrogen in an autoclave at the required temperature and pressure. Then a known amount of liquid sample is transferred into a gas buret where it is exposed to atmospheric pressure. The hydrogen desorbed displaces an equivalent amount of water from a gas collector (A). (A schematic diagram of the apparatus used is shown in Figure 1.) The displaced liquid volume is measured.

In a typical experiment, a known volume of solvent mixture is charged into the autoclave (Parr autoclave, 2×10^{-3} m^3 capacity) and maintained at the desired temperature. The empty space in the autoclave is flushed thrice with hydrogen and then the autoclave is pressurized with hydrogen to a desired pressure. The system is then allowed to equilibrate with hydrogen for about 3 h. The gas buret is also flushed with hydrogen and maintained at atmospheric pressure. The valves S_2 and S_3 are then kept closed. Then a known volume of the sample is withdrawn very slowly to the gas buret (F) with the help of the sampling valve (K). This operation was carried out carefully to avoid any gas pockets in the sampling line. As the gas buret is at a lower pressure, dissolved hydrogen gas is desorbed and collected in the gas collector (A). The volume of the desorbed gas is then measured by the displacement of water. The displaced water gets collected in a water buret (E), through the overflow device (D). The water in the gas collector is presaturated with hydrogen at atmospheric pressure. Also, a constant temperature is maintained in both the gas buret and the gas collector. The level of the liquid in the overflow device is adjusted such that it should be in horizontal line with the bottom of the dip tube in the gas collector. This is necessary to maintain the pressure in the gas buret equal to atmospheric pressure.

Table I. Comparison of the Predicted and Experimental Solubility Data of Hydrogen at Various Temperatures and 101 kPa

	solubility of hydrogen, (mol/m^3)/atm			
	in methanol		in nitrobenzene	
temp, K	exptl	predicted	exptl	predicted
298[a]	3.926	4.0	1.574	1.512
313	4.264	4.285	1.71	1.669
323	4.438	4.555	1.778	1.771
333	4.623	4.606	1.856	1.87
343	4.792	4.739	1.978	1.968

[a] Literature data: H_2-methanol, 3.917 (mol/m^3)/atm; H_2-nitrobenzene, 1.553 (mol/m^3)/atm (Gjaldbaek (*3*)).

The volume of the sample taken (v), the volume of the water displaced (V), and the height (h) of the water column above the dip tube in the gas collector were measured. The volume (at NTP) of H_2 desorbed is then calculated as

$$L = \frac{(V - v)}{v} \frac{(P - P_w - h/13.6)}{760} \frac{273}{T_w} \tag{1}$$

In order to obtain the absolute solubility of hydrogen at the autoclave pressure and temperature, one has to add a correction to the measured volume L. This correction factor corresponds to the solubility of hydrogen at the buret temperature (T_w) and a partial pressure equal to barometric pressure minus the vapor pressure of the solvent ($P - P_v$). In order to obtain this correction factor, one can extrapolate the data obtained at higher pressures and at T_w to the pressure $P - P_v$. This was simple as the data showed a linear relationship with pressure. The saturation concentration of hydrogen in the solvent used is then calculated as

$$A = (L + L')/0.022400 \tag{2}$$

where L' is the solubility (m^3 of H_2/m^3 of solvent) at T_w and a pressure $P - P_v$.

The reproducibility of the experimental measurement was checked by repeating a particular experiment 3 times. It was observed that the error in solubility values obtained was within 2–3%. Also, to check the validity of the method, we compared the results obtained for H_2–methanol and H_2–nitrobenzene with literature data (see Table I). The agreement was found to be within 2%, thus indicating correctness of the method.

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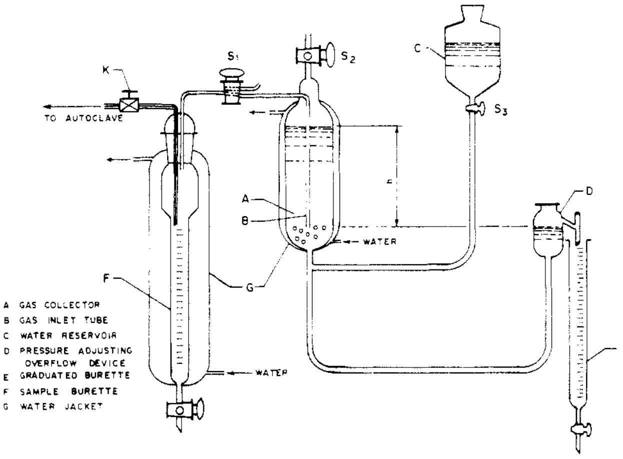

Figure 1. Schematic diagram of the solubility apparatus.

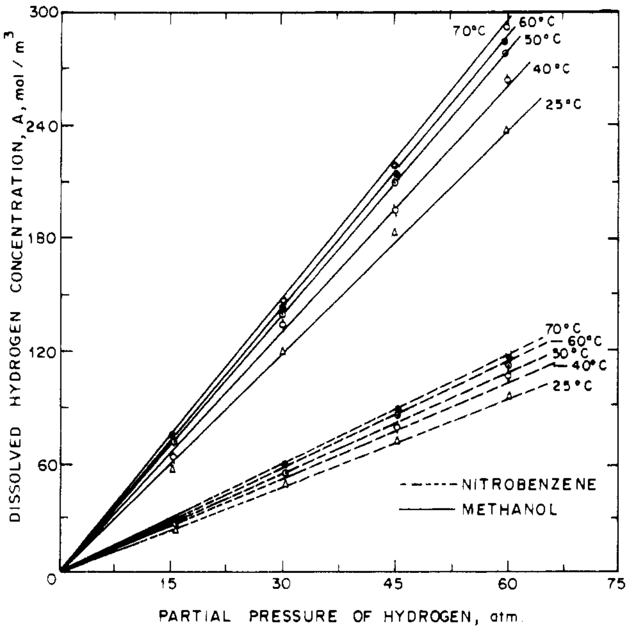

Figure 2. Effect of pressure on solubility.

Results and Discussion

The solubility of hydrogen in pure methanol and nitrobenzene was determined by the procedure described above. The effect of temperature and pressure on the solubility was investigated. The temperature was varied between 25 and 70 °C and the pressure was varied between 15 and 60 atm (1.515 × 10^3–6.060 × 10^3 kPa). The solubility of hydrogen in a mixture of methanol and nitrobenzene was also determined at 25–70 °C and 1.515 × 10^3–6.060 × 10^3 kPa partial pressure of hydrogen. The effect of nitrobenzene concentration on the solubility was studied. The nitrobenzene concentration in methanol was varied between 0 and 9.74 mol/m^3. The effect of various parameters on the solubility is discussed below.

***Effect of Pressure*.** The effect of pressure on the solubility is shown in Figure 2 for hydrogen–methanol and hydrogen–nitrobenzene systems. This figure indicates that the solubility is linearly dependent on the pressure.

***Effect of Temperature*.** The effect of temperature on the solubility of hydrogen in methanol and nitrobenzene is shown in Figure 3 as a plot of ln S vs. $1/T$ where S is the solubility at atmospheric pressure (1.01 × 10^2 kPa). It can be seen that the solubility increases with temperature for methanol and nitrobenzene. From Figure 3 the enthalpy of solution of hydrogen in methanol and nitrobenzene was found to be 3.725 and 3.810 kJ/mol, respectively.

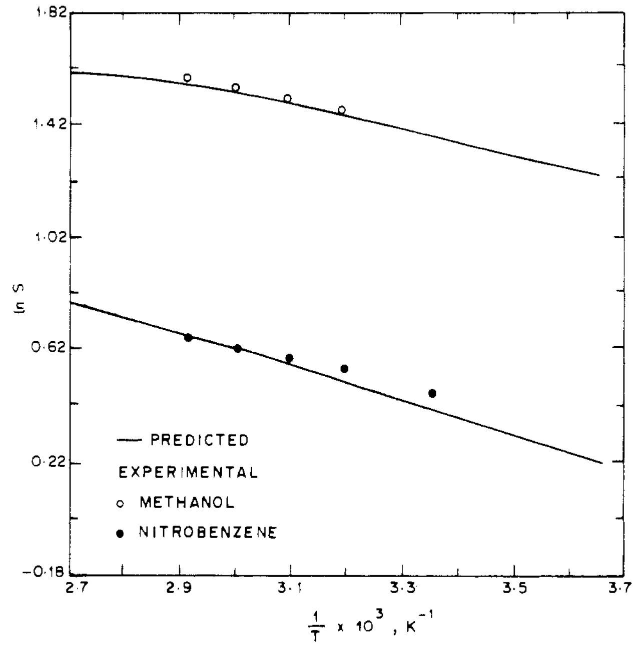

Figure 3. Effect of temperature on solubility of hydrogen in pure solvents.

Table II. Comparison of Experimental and Predicted Solubility (S) Data in Mixtures

temp, K	10^{-3}·[nitrobenzene] in methanol, mol/m^3	S,[a] (mol/m^3)/atm exptl	Hildebrand method[b]	Prausnitz and Shair method[c]
298	4.545	2.857	2.74 (4.1)	2.722 (4.7)
298	7.143	2.246	2.23 (0.7)	2.23 (0.7)
298	8.82	1.851	1.873 (−1.2)	1.874 (−1.23)
313	4.545	3.103	2.978 (4.094)	2.96 (4.6)
313	7.143	2.44	2.438 (0.08)	2.44 (0.1)
313	8.82	2.001	2.057 (−2.8)	2.059 (−2.92)
323	4.545	3.23	3.125 (3.24)	3.109 (3.75)
323	7.143	2.54	2.57 (−1.19)	2.571 (−1.2)
323	8.82	2.091	2.176 (−4.1)	2.179 (−4.2)
333	4.545	3.365	3.264 (3.01)	3.25 (3.45)
333	7.143	2.647	2.696 (−1.86)	2.69 (−1.95)
333	8.82	2.182	2.29 (−5)	2.294 (−5.2)
343	4.545	3.49	3.393 (2.8)	3.38 (3.2)
343	7.143	2.75	2.816 (−2.4)	2.82 (−2.6)
343	8.82	2.266	2.4 (−6)	2.406 (−6.2)

[a] % error in parentheses. [b] Reference 7. [c] Reference 4.

***Effect of Nitrobenzene Concentration*.** The solubility data for different concentrations of nitrobenzene in methanol are given in Table II. It is observed that the solubility decreases as the concentration of nitrobenzene increases. The relationship of solubility with temperature in a mixture is similar to that in pure solvents; i.e., solubility increases with increase in temperature.

Correlation of Data

***Pure Compounds*.** Prausnitz and Shair (*4*) have proposed the following equation on a theoretical basis for correlating the solubility of gases in liquids:

$$-\ln x_A = \ln (f_A^L/f_A) + \phi_s^2 v_A[\delta_s - \delta_A]^2/RT \qquad (3)$$

where x_A is the mole fraction of hydrogen in the liquid phase corresponding to a gas-phase partial pressure of 1 atm (1.01 × 10^2 kPa), f_A^L is the fugacity of hypothetical liquid hydrogen, f_A is the fugacity of hydrogen at 1-atm pressure, v_A is the molar volume of hypothetical liquid hydrogen, and δ_s and δ_A are the solubility parameters of the solvent and hydrogen, respectively.

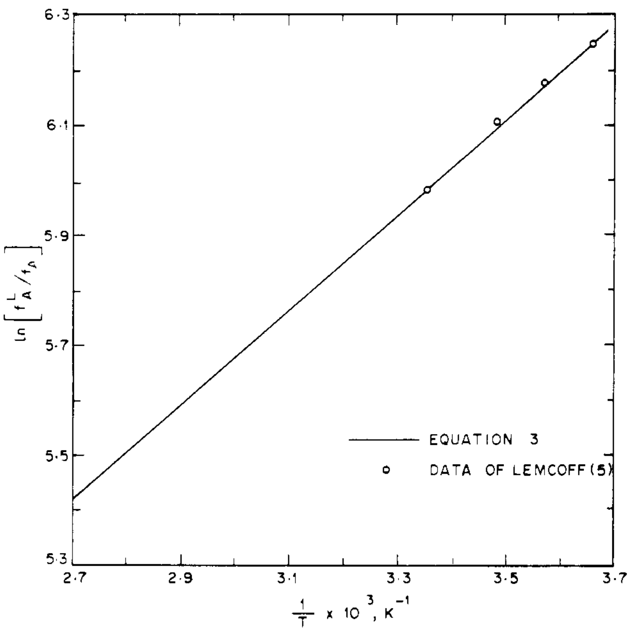

Figure 4. Temperature dependence of fugacity of hypothetical liquid hydrogen at 1 atm.

The volume fraction of hydrogen in liquid is negligible as hydrogen is sparingly soluble in most of the solvents and hence the volume fraction of solvent, ϕ_s, in eq 3 can be taken as unity.

In order to obtain a correlation of solubility over a range of temperature, it is necessary to ascribe suitable values to the parameters f_A^L, v_A, δ_s, and δ_A and also to predict changes in these parameters as a function of temperature. Some information on this aspect is available in the literature (*5*). For example, Lemcoff (*5*) used eq 3 to predict the solubility of hydrogen in a number of organic solvents. He assumed that δ_s and δ_A are independent of temperature and ascribed the value of 4.3 × 10^3 to δ_A. Other parameters, f_A^L and v_A, were then obtained by comparing eq 3 with the experimental data over a temperature range of 0–25 °C. These values for f_A^L and v_A can be used in the present work. However, as the temperature range of interest in this work is higher than 25 °C, it is necessary to correlate the data of Lemcoff (*5*) as a function of temperature. The data on fugacity (f_A^L (1 atm)) can be correlated by a linear relationship of ln f_A^L with $1/T$ to obtain the following equation:

$$\ln f_A^L = 3.111756 + 856.9404/T \tag{4}$$

Figure 4 shows the fugacity of hypothetical liquid hydrogen at various temperatures. In order to correlate v_A as a function of temperature, one first has to choose the form of the equation. For liquids below the critical temperature ln v_A varies as $(T/T_c - 1)^{2/7}$ (*6*). Although we are interested in the molar volume of hypothetical liquid hydrogen, we can assume, as an approximation, that the same type of relationship is applicable. The data of Lemcoff (*5*) for v_A fitted satisfactorily by such a relation and the correlation is

$$\ln v_A = -16.1347 + 3.0927[T/33 - 1]^{2/7} \tag{5}$$

Figure 5 shows the molar volume of hypothetical liquid hydrogen at various temperatures. The solubility parameter of the solvents can be correlated as a function of temperature by the following equation (*6*):

$$\delta_s = (\Delta H_v - RT)/v_s \tag{6}$$

where ΔH_v is the heat of vaporization and v_s is the molar volume of the solvent. For methanol, the solubility parameter needs to be further corrected by the method given by Lemcoff (*5*) since δ_s for methanol is far greater than 9.

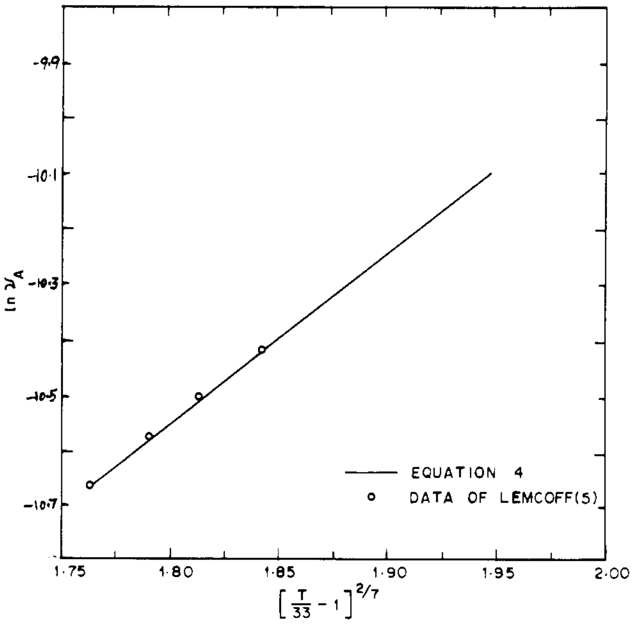

Figure 5. Temperature dependence of molar volume of hypothetical liquid hydrogen.

Table III. Parameters Required for Prediction of Solubility

temp, K	$\ln f_A^L$ (1 atm)	$10^5 v_A$, m^3/mol	$10^{-4}\delta_s$, J$^{1/2}$/m$^{3/2}$ methanol[a]	$10^{-4}\delta_s$, J$^{1/2}$/m$^{3/2}$ nitrobenzene	$10^{-3}\delta_A$, J$^{1/2}$/m$^{3/2}$ methanol	$10^{-3}\delta_A$, J$^{1/2}$/m$^{3/2}$ nitrobenzene
298	5.987	2.687	2.122	2.044	5.355	4.435
313	5.85	2.937	2.131	2.041	5.564	4.607
323	5.765	3.111	2.137	2.039	5.7	4.719
333	5.685	3.290	2.143	2.036	5.829	4.828
343	5.61	3.490	2.149	2.034	5.958	4.934

[a] Corrected according to Lemcoff (*5*).

$$(\delta_s)_{cor} = \frac{\delta_s}{1.772 \log [\delta_s - \delta_A] - 0.509} \tag{7}$$

where the term δ_s on the right-hand side of eq 7 represents an uncorrected value obtained from eq 6.

Finally, we require the value of δ_A in order to have a correlation for solubility. Since the temperature range investigated in this study is above the critical temperature of hydrogen, the conventional method for calculating the value of δ_A cannot be used. No satisfactory theory is applicable for predicting liquid-state properties of a gas at a temperature far greater than its critical temperature. δ_A may be viewed as a correlating constant which is a function of temperature. Some authors assumed a δ_A value between 4.296 × 10^3 and 1.043 × 10^4; for example, 4.296 × 10^3 by Hildebrand (*7*) and Lemcoff (*5*), 6.649 × 10^3 by Prausnitz and Shair (*4*), and 1.043 × 10^4 by Gjaldbaek (*3*). In the present work we assumed that δ_A varies with temperature by an equation similar to eq 6

$$\frac{(\delta_A)_T}{(\delta_A)_{298}} = \frac{(\Delta H_v)_A - RT}{(\Delta H_v)_A - 298R} \tag{8}$$

where $(\delta_A)_{298}$ is the solubility parameter for hydrogen at 298 K and $(\Delta H_v)_A$ is 905 J/mol. Thus, the parameter $(\delta_A)_{298}$ required for solubility predictions was obtained by fitting the data at 298 K. In this work the values of $(\delta_A)_{298}$ obtained are 4.435 × 10^3 for nitrobenzene and 5.355 × 10^3 for methanol. The parameters f_A^L, v_A, δ_s, and δ_A at various temperatures are given in Table III.

Table IV. Comparison of Enthalpy of Solution

system	enthalpy of soln, J/mol exptl	 predicted
hydrogen-methanol	3725	3215
hydrogen-nitrobenzene	3810	4980

The solubility data predicted by the correlation given by eq 3 are presented in Table II and compared with the experimental data. The comparison is also shown graphically in Figure 3. The correlation agrees well with the experimental data within a maximum error of 4.1%, a minimum error of 0.42%, and an average error of 2% for nitrobenzene. Similarly for methanol a maximum error of 1.6%, a minimum error of 0.36%, and an average error of 0.85% were observed. Also, the predicted enthalpy of solution can be compared with the experimental value and these are given in Table IV.

Correlation for Mixtures. For predicting the solubility of hydrogen in a mixture of solvents, one can use a method similar to that proposed by Prausnitz and Shair (*4*). According to the theory proposed by these authors, the solubility in a mixture is given by

$$-(\ln x_A)_{mix} = \ln f_A^L + v_A(\bar{\delta} - \bar{\delta}_A)^2/RT \tag{9}$$

where $\bar{\delta}$ and $\bar{\delta}_A$ are the average solubility parameters defined as

$$\bar{\delta} = \phi_i\delta_i \tag{10}$$

$$\bar{\delta}_A = \phi_i(\delta_A)_i \tag{11}$$

where

$$\phi_i = x_iv_i/\sum x_iv_i \tag{12}$$

Hildebrand et al. (*7*) suggested that the solubility of a gas in a binary mixture of solvents can be estimated by the following expression:

$$(\ln x_A)_{mix} = \phi_1 \ln x_{A,1} + \phi_2 \ln x_{A,2} - v_A\beta_{12}\phi_1\phi_2 \tag{13}$$

where

$$\beta_{12} = (\delta_1 - \delta_2)^2/RT \tag{14}$$

The solubility of hydrogen in a mixture of methanol-nitrobenzene was predicted with eq 9 and 13. For this purpose the molar volume of the mixture determined experimentally for different concentrations was used. The predicted solubility data were compared with the experimental values and are presented in Table II. For hydrogen-methanol and hydrogen-nitrobenzene systems the agreement between both the correlations and the experimental data was quite satisfactory. The maximum error was found to be 6.2%. The variation of the solubility with mole fraction of nitrobenzene in a mixture is shown in Figure 6.

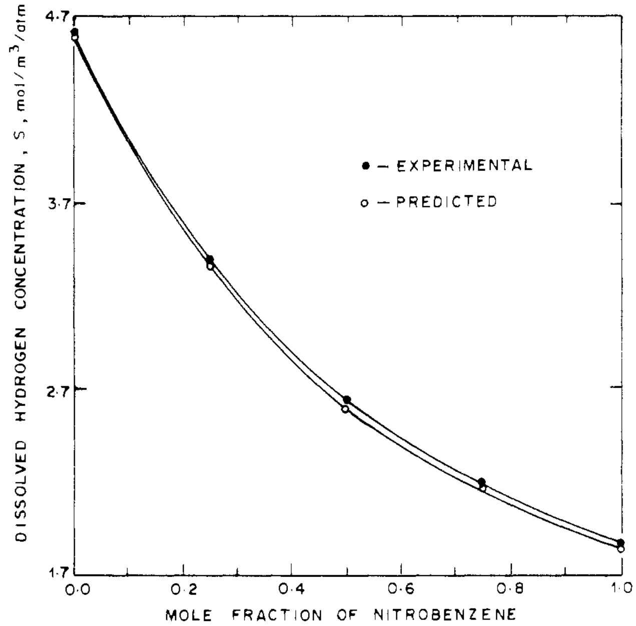

Figure 6. Solubility of hydrogen in mixture of nitrobenzene and methanol.

Conclusion

The solubility of hydrogen in mixtures of methanol and nitrobenzene and pure solvents was determined. These data were correlated by using the equations developed for the theoretical prediction of solubility. These correlations agree with the experimental data within 6.2% error over the range of temperatures investigated.

Glossary

A	hydrogen concentration at the autoclave pressure and temperature, mol/m^3
f_A^L	fugacity of hypothetical liquid hydrogen at 1 atm
f_A	fugacity of pure gas at 1 atm
h	height of water column in the gas collector
ΔH	enthalpy of solution, J/mol
ΔH_v	heat of vaporization, J/mol
L	solubility of hydrogen through eq 1, m^3/m^3
L'	correction factor for solubility, m^3/m^3
P	barometric pressure, mmHg
P_v	vapor pressure of solvent, mmHg
P_w	vapor pressure of water, mmHg
R	gas constant, J/(mol K)
S	dissolved hydrogen concentration at 1-atm partial pressure of hydrogen, (mol/m^3)/atm
T	temperature, K
T_w	temperature of gas buret, K
v	volume of sample taken, m^3
V	volume of displaced water, m^3
v_A	molar volume of hydrogen, m^3/mol
v_i	molar volume of component i, m^3/mol
v_s	molar volume of solvent, m^3/mol
x_A	mole fraction of hydrogen in the liquid
x_i	mole fraction of component i
δ_A	solubility parameter of hydrogen, J$^{1/2}$/m$^{3/2}$
δ_s	solubility parameter of solvent, J$^{1/2}$/m$^{3/2}$
ϕ_1	volume fraction of component 1
ϕ_2	volume fraction of component 2
ϕ_s	volume fraction of solvent
ϕ_i	volume fraction of component i
β_{12}	parameter defined through eq 14
$\bar{\delta}'$	average solubility parameter of solvent defined through eq 10
$\bar{\delta}_A'$	average solubility parameters of hydrogen defined through eq 11

Registry No. H_2, 1333-74-0; methanol, 67-56-1; nitrobenzene, 98-95-3.

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