Solubility of Hydrogen in α-Methylstyrene and Cumene at Elevated Pressure

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The solubility of hydrogen in the liquid phase is an important parameter which influences the rate of reaction in three-phase catalytic hydrogenation. Experimental data for the solubility of hydrogen in α-methylstyrene and cumene at elevated pressure are presented. The solubility of hydrogen in α-methylstyrene is reported at temperatures of 308 K and 323 K and pressures to 13 MPa. Data for cumene are reported at a temperature of 323 K and pressures to 12 MPa. The solubility data are correlated with the Peng−Robinson equation of state using a single adjustable interaction parameter and a modified α function for hydrogen.

Introduction

Three-phase catalytic hydrogenation (TPCH) is a widely employed process for the hydrogenation of relatively non-volatile liquid hydrocarbons in the presence of a solid catalyst.[1] An intrinsic feature of TPCH is the interphase transport of hydrogen through the liquid phase to the catalyst surface where the reaction actually takes place. Mass transfer limitations, in combination with the typically low solubility of hydrogen in the liquid phase, significantly reduce the rate of reaction in TPCH. These limitations can be overcome to some extent by conducting the reaction at higher pressure and/or improving the method of contact between the gas and liquid phases. Higher pressure increases the solubility of hydrogen in the liquid phase.[2] Gas−liquid interaction is often more efficient if the liquid flows over the solid catalyst in the form of thin films, as in trickle bed reactors.[3]

In a recent innovation, Devetta et al.[4] have shown that the use of supercritical carbon dioxide as a reaction solvent can significantly increase the rate of reaction in TPCH. This effect is mainly attributed to the modification of phase equilibria, particularly with respect to the concentration of hydrogen in the liquid phase. In their work, phase equilibrium calculations revealed that the addition of supercritical carbon dioxide was accompanied by an increase in the hydrogen/reactant ratio in the liquid phase. The study by Devetta and co-workers highlights the importance of understanding phase equilibria when interpreting reaction rate data for multiphase systems containing carbon dioxide at elevated pressure. Moreover, phase equilibrium calculations must be performed in conjunction with kinetic measurements in order to estimate concentration terms which appear in kinetic rate expressions.

In this work, we present experimental data for the high-pressure solubility of hydrogen in α-methylstyrene and cumene, the latter being the hydrogenated derivative of α-methylstyrene. These organic components are considered to be representative of a typical TPCH system in view of their relatively high boiling points and relevance to the

petrochemical industry. The experimental data are correlated with the Peng−Robinson (PR) equation of state[5] and the interaction parameters for each binary system are obtained by regression. This information is required in the subsequent calculation of phase equilibrium data pertaining to the multicomponent system containing supercritical carbon dioxide.

Experimental Section

Equipment. A schematic diagram of the experimental apparatus used in this work is shown in Figure 1. A circulation type apparatus was used in which the liquid phase was recirculated, sampled, and analyzed. The equilibrium cell consisted of a high pressure sight gauge with an internal volume of approximately 60 cm³ (Jerguson, 13-R-32). The temperature in the equilibrium cell was monitored with a type K thermocouple. The equilibrium cell was immersed in a water bath for which the temperature was maintained to ±0.2 K with a heater/circulator (Thermoline, Unistat 130). The system pressure was measured with a pressure transducer with an uncertainty of ±0.035 MPa. (Druck, PDCR 911). The liquid phase was withdrawn from the bottom of the equilibrium cell and recirculated to the top using a metering pump (Eldex, B-100-S-2-CE). The solvent trap consisted of a 50 cm³ sample cylinder. The outlet of the solvent trap was connected to an inverted buret (0.05 mL graduations) which was used to determine the quantity of hydrogen dissolved in the liquid-phase sample.

Procedure. Approximately 20 mL of α-methylstyrene (99%, Sigma-Aldrich) or cumene (99%, Sigma-Aldrich) was added to the equilibrium cell followed by purging of the cell and connecting lines with hydrogen (99.98%, Linde Gas) at low pressure (~0.5 MPa) to displace any air present. The liquid phase was degassed by recirculating it during the purging step. The equilibrium cell was filled with hydrogen to the desired pressure and then isolated by closing valves V2 and V3. The liquid phase was then recirculated in order to attain equilibrium between the liquid and vapor phases. During the initial stages of recirculation, a slight reduction in pressure occurred due to the dissolution of hydrogen in the liquid phase. The

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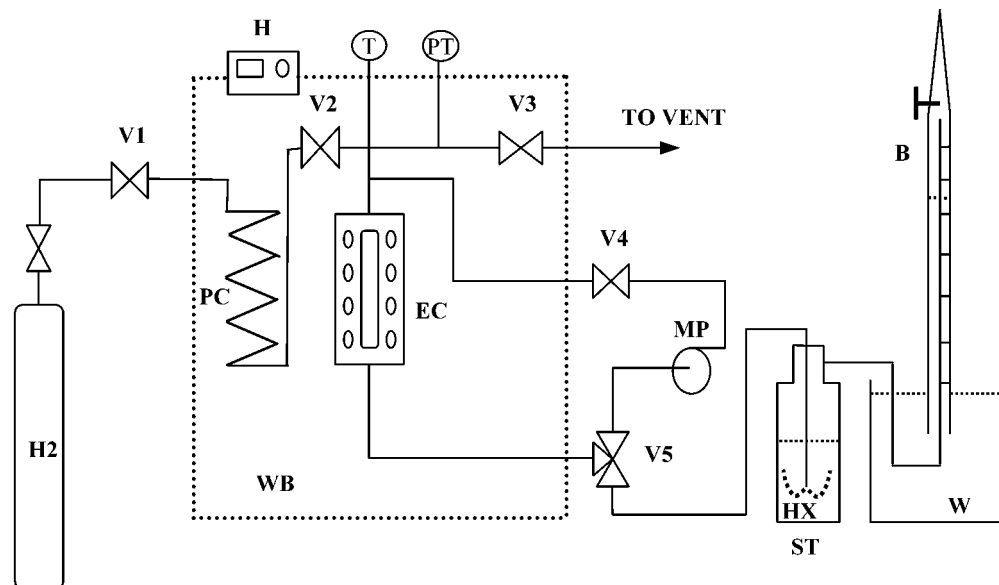
Figure 1. Schematic diagram of the experimental apparatus: (B) buret, (EC) equilibrium cell, (H) heater, (H2) hydrogen cylinder, (HX) hexane, (MP) metering pump, (PC) preheating coil, (PT) pressure transducer, (ST) solvent trap, (T) thermocouple, (V) valve, (W) water, and (WB) water bath.

pressure was maintained at the desired value by the addition of hydrogen through valve V2. It was observed that the temperature and pressure readings of the system attained stable values within a period of 15 min. However, the attainment of equilibrium was confirmed by monitoring the composition of the liquid phase over time. Over the range of conditions examined, the duration of time required for the system to reach equilibrium was typically less than 30 min.

A small sample of the liquid phase was removed from the equilibrium cell via valve V5. The hydrogen dissolved in the sample was separated from the liquid component using a solvent trap filled with a known quantity of hexane. The gas which evolved from the sample was allowed to pass into a graduated buret where the volume displacement of water was recorded. Since the solvent trap was operated at near atmospheric pressure, the actual quantity of hydrogen collected from the sample was calculated using the ideal gas equation as follows

$$n_{H} = \frac{1}{RT}(P_{f}V_{f} - P_{i}V_{i}) \qquad (1)$$

where n_{H} is the number of moles of hydrogen and P and V are the pressure and gas volume in the solvent trap, respectively. The subscripts i and f refer to the initial and final conditions in the solvent trap. As can be seen from Figure 1, the gas space above the hexane in the solvent trap is directly connected to the gas space at the top of the buret. The pressure in the solvent trap was therefore deduced from the height of water in the buret. It is important to note that each gas volume term in eq 1 is the combined volume of gas in the solvent trap and the buret, corrected for the amount of hexane added initially to the solvent trap. In the case of V_{f}, a correction is also made for the amount of α-methylstyrene /cumene collected in the solvent trap as well as the volume displacement of water in the buret. Each pressure term in eq 1 is corrected for the partial pressure of hexane which is assumed to be equal to its vapor pressure at the prevailing temperature.

In a typical experiment, a sufficient amount of liquid was removed from the equilibrium cell so as to displace the

water level in the buret by 1 to 3 mL. The hexane in the solvent trap was also saturated with hydrogen prior to sampling. This procedure was adopted to prevent the absorption of hydrogen, from the sample, into the hexane. The drop in pressure in the equilibrium cell was less than 1 bar during the sampling procedure. After each sample was taken, the desired pressure was restored in the equilibrium cell followed by recirculation of the liquid phase for a period of at least 30 min.

The liquid component remaining in the connecting line between valve V5 and the solvent trap was recovered using a rinsing procedure. The rinse solution was combined with the solution in the solvent trap. The combined solution was then analyzed by gas chromatography to determine the total mass of α-methylstyrene or cumene associated with the hydrogen from the sample. The solubility of hydrogen in the liquid phase was determined from the average of at least three measurements, with a relative standard deviation (RSD) of less than 3%. The RSD was calculated with respect to the ratio of α-methylstyrene or cumene to hydrogen in the sample. The solubility data are reported as the mole fraction of hydrogen in the liquid phase. The estimated uncertainty in the liquid-phase mole fraction is less than 0.003.

Results and Discussion

Experimental data for the solubility of hydrogen in α-methylstyrene and cumene are listed in Table 1. The data for α-methylstyrene were measured at 308 K and 323 K and for pressures to 13 MPa. The data for cumene were measured at 323 K and for pressures to 12 MPa. Herskowitz et al.[6] have also reported solubility data for hydrogen in α-methylstyrene (303 K, 333 K, and 373 K) and cumene (333 K and 373 K) in the range of pressure from 0.8 to 7.0 MPa. A comparison between the various data sets is shown in Figures 2 and 3. The published data for α-methylstyrene at 303 K have been omitted from Figure 2 to improve the clarity of the diagram. It can be seen that a linear relationship exists between pressure and solubility and this is consistent with Henry's law for sparingly soluble gases in liquids. The data indicate that the solubility of hydrogen
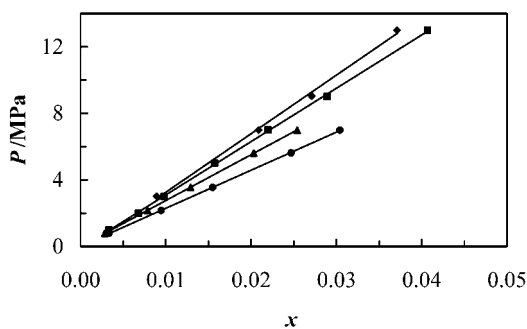
Figure 2. Solubility of hydrogen in α-methylstyrene: (◆) 308 K, this work; (■) 323 K, this work; (▲) 333 K, Herskowitz et al.;[6] (●) 373 K, Herskowitz et al.[6] The solid lines represent lines of best fit.
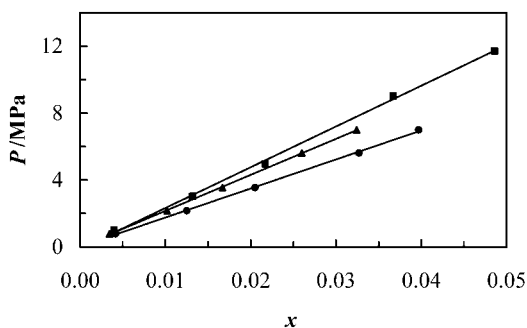

Figure 3. Solubility of hydrogen in cumene: (■) 323 K, this work; (▲) 333 K, Herskowitz et al.;[6] (●) 373 K, Herskowitz et al.[6] The solid lines represent lines of best fit.

Table 1. Mole Fraction Solubility of Hydrogen (x) in α-Methylstyrene and Cumene

P/MPa	x	P/MPa	x
	α-Methylstyrene, $T = 308$ K		
3.02	0.0089	9.03	0.0271
7.00	0.0209	13.00	0.0371
	α-Methylstyrene, $T = 323$ K		
1.00	0.0033	7.01	0.0220
2.00	0.0068	9.01	0.0289
3.00	0.0098	13.00	0.0407
5.01	0.0157		
	Cumene, $T = 323$ K		
1.02	0.0040	9.02	0.0367
3.01	0.0132	11.70	0.0486
4.97	0.0217		

increases with increasing temperature at constant pressure. This trend is commonly observed in binary systems consisting of hydrogen and an organic solvent.[7-10]

The experimental solubility data, including the data of Herskowitz and co-workers, were correlated with the PR equation of state using a single adjustable interaction parameter (k_{ij}). A bubble-point calculation procedure was employed in which the vapor phase composition and the system pressure were calculated from the liquid-phase composition and the system temperature. The optimum value of k_{ij} for each isotherm of data was obtained by minimizing the sum of squared relative deviations (SSRD) with respect to pressure

$$\text{SSRD} = \sum_i^N \left(\frac{P_{\text{calcd}} - P_{\text{exptl}}}{P_{\text{exptl}}} \right)^2_i \qquad (2)$$

where N is the number of data points, P_{calcd} and P_{exptl} are the calculated and experimental values of pressure, respectively. The attractive (a) and repulsive (b) parameters

Table 2. Critical Properties and Acentric Factors Used in the PR Equation of State

component	MW	T_c/K	P_c/MPa	ω
hydrogen[a]	2.016	32.98	1.293	−0.217
α-methylstyrene [b]	118.18	654	3.36	0.3273
cumene[b]	120.19	631.15	3.2088	0.3377

[a] Data are from Poling et al.[13]   [b] Data are from Daubert and Danner.[14] Critical properties and ω for α-methylstyrene are estimated values. Critical properties for cumene are experimental values. ω for cumene is an estimated value.

required in the PR equation of state were calculated using conventional mixing rules:

$$a = \sum_i \sum_j x_i x_j (1 - k_{ij})(a_i a_j)^{1/2} \qquad (3)$$

$$b = \sum_i x_i b_i \qquad (4)$$

Values of a and b were calculated for each phase independently, although the same value of k_{ij} was used for each phase. Note that x in eqs 3 and 4 refers to both vapor and liquid composition. The pure component parameters (a_i and b_i) were calculated with the conventional equations. The temperature dependence of a_i in the PR equation of state is expressed by the α function

$$\alpha(T) = [1 + m(1 - T_r^{1/2})]^2 \qquad (5)$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \qquad (6)$$

where T_r is the reduced temperature and ω is the acentric factor. These equations were originally developed to reproduce the vapor pressures of pure nonpolar substances. For quantum gases[11] such as hydrogen, eqs 5 and 6 may yield less reliable estimates of α, particularly at reduced temperatures greater than 1.0. Fu and Tan[12] have evaluated a number of empirical expressions for calculating the value of α for pure hydrogen. They propose the following modified α function, for hydrogen, for use with the PR equation of state:

$$\alpha(T) = [1 + 0.30298(1 - T_r^{1/2}) + 0.07889(1 - 1/T_r)]^2 \qquad (7)$$

The critical properties of the various components, required for the correlation of the data, are listed in Table 2. Optimized values of k_{ij} are presented in Table 3 in which it can be seen that the modified α function for hydrogen yields a better fit of the experimental data for all of the temperatures considered. For the standard α function, the k_{ij} values (0.4 to 0.5) are similar in magnitude to those obtained for other nonpolar liquids.[2,15] It is noted that the k_{ij} values obtained with the modified α function are all negative.

Correlation results obtained with the PR equation of state and the modified α function are shown in Figures 4 and 5. The results are presented in terms of the relative deviations (RD) of the calculated pressures from the experimental pressures. Overall, the PR equation of state provides a satisfactory correlation of the experimental data. It is evident from Figure 5, however, that the PR equation of state is less satisfactory for cumene at low pressure (<2.0 MPa). The average absolute relative deviations (AARD), with respect to pressure, for α-methylstyrene range from 1.5 to 2.0% while those for cumene range from 2.8 to 4.0%. If the standard α function is used for hydrogen, the AARDs

Table 3. Optimized Values of k_{ij} from the PR Equation of State

system	T/K	k_{ij}	SSRD[b]
Standard α Function (Eq 5)			
hydrogen + α-methylstyrene	303	0.4770[a]	0.0028
	308	0.4970	0.0032
	323	0.5273	0.0048
	333	0.5034[a]	0.0026
	373	0.5681[a]	0.0032
hydrogen + cumene	323	0.4201	0.0146
	333	0.4085[a]	0.0084
	373	0.4308[a]	0.0096
Modified α Function (Eq 7)			
hydrogen + α-methylstyrene	303	−0.0708[a]	0.0016
	308	−0.0301	0.0019
	323	−0.0231	0.0032
	333	−0.1200[a]	0.0016
	373	−0.1161[a]	0.0022
hydrogen + cumene	323	−0.2585	0.0120
	333	−0.3347[a]	0.0069
	373	−0.4778[a]	0.0083

[a] k_{ij} regressed from the experimental data of Herskowitz et al.[6]
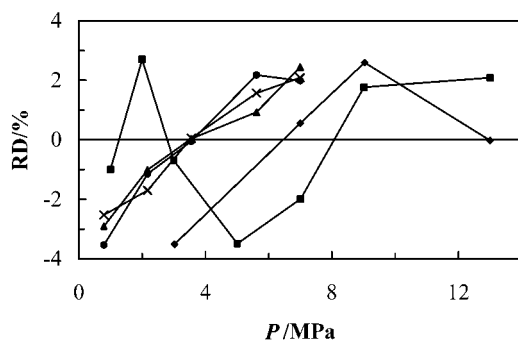[b] Sum of squared relative deviations (eq 2).

Figure 4. Correlation results for hydrogen + α-methylstyrene from the PR equation of state using the modified α function for hydrogen: (×) 303 K; (◆) 308 K; (■) 323 K; (▲) 333 K; (●) 373 K.
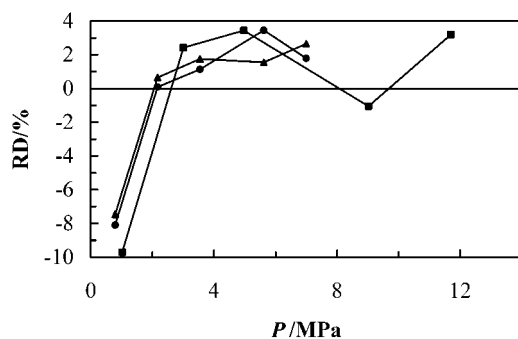

Figure 5. Correlation results for hydrogen + cumene from the PR equation of state using the modified α function for hydrogen: (■) 323 K; (▲) 333 K; (●) 373 K.

are around 30% and 7% greater for α-methylstyrene and cumene, respectively.

Conclusions

Experimental data have been obtained for the solubility of hydrogen in α-methylstyrene and cumene at elevated pressure. A linear relationship exists between pressure and solubility over the range of pressure investigated for both components. The use of a single adjustable interaction parameter with the PR equation of state provides a satisfactory correlation of the data.

Literature Cited

(1) Ramachandran, P. A.; Chaudhari, R. V. *Three-Phase Catalytic Reactors*; Gordon and Breach: New York, 1983.

(2) Gao, W.; Robinson, R. L.; Gasem, K. A. M. Solubilities of Hydrogen in Hexane and of Carbon Monoxide in Cyclohexane at Temperatures from 344.3 to 410.9 K and Pressures to 15 MPa. *J. Chem. Eng. Data* **2001**, *46*, 609−612.

(3) Al-Dahhan, M. H.; Larachi, F.; Dudukovic, M. P.; Laurent, A. High-Pressure Trickle-Bed Reactors: A Review. *Ind. Eng. Chem. Res.* **1997**, *36*, 3292−3314.

(4) Devetta, L.; Giovanzana, A.; Canu, P.; Bertucco, A.; Minder, B. J. Kinetic Experiments and Modeling of a Three-Phase Catalytic Hydrogenation Reaction in Supercritical CO_2. *Catal. Today* **1999**, *48*, 337−345.

(5) Peng, D.-Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59−64.

(6) Herskowitz, M.; Wisniak, J.; Skladman, L. Hydrogen Solubility in Organic Liquids. *J. Chem. Eng. Data* **1983**, *28*, 164−166.

(7) Gao, W.; Robinson, R. L.; Gasem, K. A. M. High-Pressure Solubilities of Hydrogen, Nitrogen, and Carbon Monoxide in Dodecane from 344 to 410 K at Pressures to 13.2 MPa. *J. Chem. Eng. Data* **1999**, *44*, 130−132.

(8) d'Angelo, J. V. H.; Francesconi, A. Z. Gas−Liquid Solubility of Hydrogen in n-Alcohols ($1 \leq n \leq 4$) at Pressures from 3.6 MPa to 10 MPa and Temperatures from 298.15 K to 525.15 K. *J. Chem. Eng. Data* **2001**, *46*, 671−674.

(9) Parent, J. S.; Rempel, G. L. Solubility of Hydrogen in Chlorobenzene. *J. Chem. Eng. Data* **1996**, *41*, 192−194.

(10) Brunner, E. Solubility of Hydrogen in 10 Organic Solvents at 298.15, 323.15, and 373.15 K. *J. Chem. Eng. Data* **1985**, *30*, 269−273.

(11) Gunn, R. D.; Chueh, P. L.; Prausnitz, J. M. Prediction of Thermodynamic Properties of Dense Gas Mixtures Containing One or More of the Quantum Gases. *AIChE J.* **1966**, *12*, 937−941.

(12) Fu, M.-S.; Tan, C.-S. Solubility of Hydrogen in a Mixture of n-Hexane and Dicyclopentadiene from 313 to 363 K and from 2.0 to 5.5 MPa. *Fluid Phase Equilibr.* **1994**, *93*, 233−247.

(13) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2001.

(14) Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation*; Hemisphere Publishing Corporation: New York, 1989.

(15) Ohe, S. *Vapour-Liquid Equilibrium Data at High Pressure*; Kodansha: Tokyo, 1990.