# Experimental and Modeling of the Propene Solubility in the Heptane and Methylbenzene Solvents

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ABSTRACT: To estimate the amount of dissolved propene gas in various industrial solvents especially in the early time of polymerization in slurry-phase propene polymerization and consequently achieve real polymer productivity, the precise experimental solubility data are needed. The solubility of propene in methylbenzene and heptane was measured at pressures from (0.13 to 1.27) MPa and temperatures ranging from (313 to 359) K. A static apparatus is used to measure the experimental data. The experimental data are modeled using the Peng−Robinson cubic equation of state (PR CEOS) with the van der Waals (vdW) mixing rule with two adjustable parameters. The modeling results show that the PR CEOS is capable to represent the experimental data well.
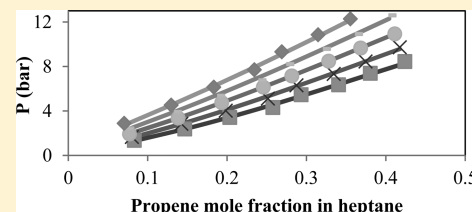
INTRODUCTION

The importance of the equilibrium data has provided an impetus from past to present to find this data because of its utilization in the design of many petroleum, gas, and petrochemical processes such as separation, absorption, multiphase fluid transport, etc.[1] One of the main applications of the propene solubility data is the mass transfer calculation between gas−liquid phases and evaluation of various solvents' performance in the slurry-phase propene polymerization process. In fact, polypropene (PP) is the second-most widely used commodity thermoplastic in the world in which the slurry-phase process makes a large contribution in the PP production process still now.[3,4] In the slurry-phase PP process, the early stages of polymerization and prepolymerization step are mainly affected on final properties of produced PP particles. Thus, the propene solubility data must be known to understand about mass transfer calculations in these two essential steps.[2−4] Consequently, the solubility data are needed for catalyst activity evaluation, productivity of polymer produced, reactor design, simulation, control, and analysis in the whole slurry-phase polymerization processes. Since the overall polymer productivity in a slurry-phase PP plant is normally related to the total mass of propene consumed in the reactor, it is crucial to know the exact concentration of propene gas in those applicable solvents such as heptane, hexane, methylbenzene, and the other ones.[2−4] Unfortunately, there is not enough solubility data of propene gas to estimate the polymerization kinetics parameters at different temperatures and pressures in slurry-phase PP process especially for using laboratory experiments.[3,4] Azarnoosh and Mcketta (1959)[5] are possibly the first researchers who studied the solubility of propene. They obtained solubility data in a wide range of temperature and pressure for propene−water system. Konobeev and Lyapin (1967)[6] obtained the solubilities of ethylene and propene gas in methylbenzene which our data is close to their results. In 1990, Hayduk and Wong[7] studied solubility of propene in octane and various polar components such as acetone, acetic acid, etc. They explained the different solubilities of various components by molecular interaction

parameter (MIP) and identified several different types of molecular interactions.

In 1996, Li et al.[8] presented equilibrium solubility of propene in liquid hexane with and without solid PP powder, under pressures from 0.2 MPa to about 1 MPa and temperatures from (313 to 353) K. In the case of the mixture containing up to 30 wt % PP powder, they found that the solubility values were not affected by the presence of solids.

Atiqullah et al. (1998)[2] applied SRK and PR CEOS for modeling the solubility of ethylene and propene in methylbenzene by using the experimental data of Konobeev and Lyapin.[6] Their results showed more accurate prediction at pressure and temperature below 5 atm and 50 °C, respectively. They recommended carrying out the metallocene-catalyzed ethylene and propene slurry polymerization below the mentioned conditions in order to obtain more accurate data of catalyst activity versus polymerization time.

Sato et al. (2001)[9] measured solubility of propene in PP powder without using any solvent. Actually, their results showed the sorption effects of swelling PP in propene gas which can be considered in gas and slurry phase polymerization. On the other hand, according to the results found by Li et al.,[8] the solubility data may not be significantly deviated for slurry-phase in the presence of polymer particles.

Dariva et al. (2003)[1] obtained experimental data of propene in methylbenzene and isodecane. They believed and stated that the observed differences between their results with previous available data including solubility data presented by Konobeev and Lyapin[6] "are mainly due to the different measuring techniques used in the two independent studies". In addition, they achieved the activity coefficients by applying two different models including an empirical model and the Wilson excess Gibbs free energy model.
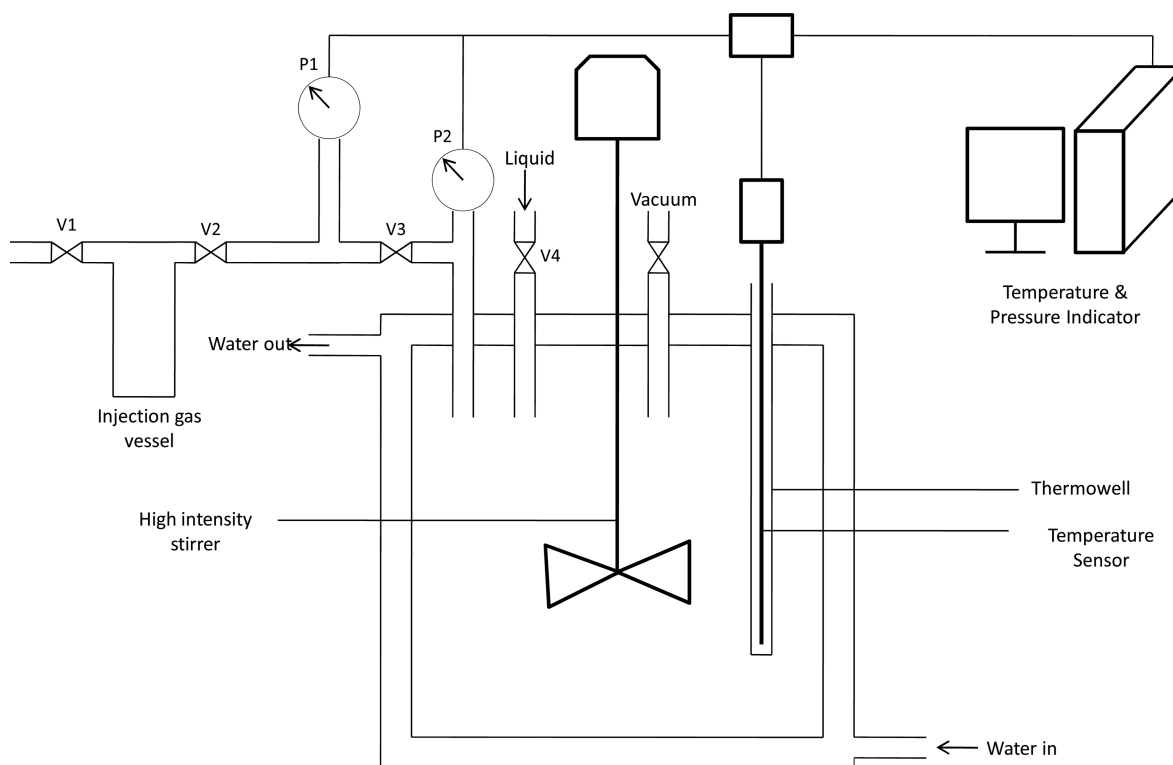
Figure 1. Propene solubility measurement apparatus in this work.

The assurance experimental solubility data of propene in hetpane in wide ranges of temperature and pressure close to that of slurry phase PP polymerization process, i.e., up to 359 K and 1.27 MPa, is an interesting scientific and technical issues still now. In addition, the presented experimental data is considered and compared with predicted results of appropriate thermodynamic models.

■ EXPERIMENTAL SECTION

Materials. Propene (mole fraction purity 0.999) was purchased from technical gas services, heptane (mass fraction purity ≥ 0.99) from Merck, and methylbenzene (mass fraction purity ≥ 0.998) from Dr. Mojallali Chemical Complex Co. (Iran) were prepared.

Apparatus and Procedure. In this work, the solubility of the propene gas in the mentioned solvents was measured using a static apparatus similar to the setup used by Mazloumi et al.[10] The schematic of the solubility measurement apparatus is shown in Figure 1. The essential steps of the measurements are as following: (a) feeding a certain amount of the solvent in the equilibrium cell, (b) injecting of the known amount of gas into the cell, and (c) recording the equilibrium pressure and temperature automatically to reach stable conditions. The recorded data were applied to calculate the solubility of propene gas in each solvent. The apparatus is consisting of three major parts: an equilibrium cell with a high intensity stirrer (stirrer speed up to 2000 rpm) and a volume of approximately 200 cm³, an injection gas vessel with approximately 70 cm³ volume, and a thermostatic water bath. The pressure of the equilibrium cell is measured by means of a pressure transducer ranging from (0 to 1.6) MPa with uncertainty of ± 0.0016 MPa (BD Sensors, Germany). The pressure of the injection gas vessel is measured using a pressure transducer (Trafag Sensors, Swiss) ranging from (0 to 2.5) MPa with uncertainty of ± 0.0025 MPa. The temperature of the
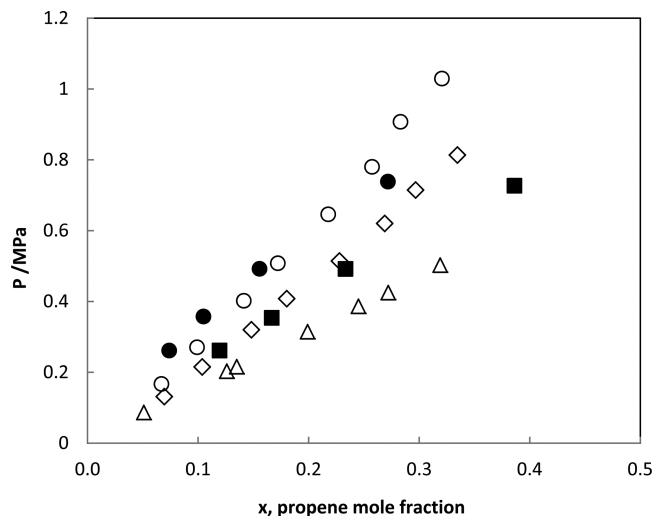

Figure 2. Experimental data of propene solubility in methylbenzene. (○, T = 336 K, this work; ●, T = 333 K;[6] ◇, T = 314 K, this work; ■, T = 313 K;[6] △, T = 313 K;[1]).

equilibrium cell is monitored and controlled with ± 0.1 °C accuracy. The weight of the injected solvent is measured with a weight balance with an accuracy of 0.01 g.

First, the equilibrium cell is evacuated several times; then the approximate volume of 30 cm³ solvent is injected into the cell. After achieving to desired temperature of the cell, the propene gas is injected into the cell from the injection gas vessel connected to the gas cylinder. The accuracy of the ambient temperature measurement is ± 0.2 °C. The stirrer is turned on and after about 30 min the vapor−liquid equilibrium was attained. The equilibrium pressure and temperature of the cell are recorded. The propene mole fraction (x_1) in each solvent is calculated as follows:

Table 1. Obtained Experimental Data of Propene Solubility in Methylbenzene[a]

T = 313.4 K		T = 324.8 K		T = 336.2 K	
x_{C3H6}	P/MPa	x_{C3H6}	P/MPa	x_{C3H6}	P/MPa
0.069 ± 0.002	0.131	0.068 ± 0.002	0.149	0.067 ± 0.002	0.167
0.104 ± 0.002	0.215	0.101 ± 0.002	0.243	0.099 ± 0.002	0.271
0.148 ± 0.003	0.320	0.145 ± 0.003	0.359	0.141 ± 0.003	0.402
0.180 ± 0.004	0.408	0.176 ± 0.004	0.457	0.172 ± 0.004	0.508
0.228 ± 0.004	0.514	0.223 ± 0.004	0.578	0.218 ± 0.005	0.646
0.269 ± 0.005	0.620	0.263 ± 0.005	0.699	0.257 ± 0.005	0.780
0.297 ± 0.005	0.715	0.290 ± 0.005	0.810	0.283 ± 0.005	0.908
0.334 ± 0.006	0.813	0.327 ± 0.006	0.919	0.320 ± 0.006	1.029
T = 347.6 K				T = 359.1 K	
x_{C3H6}	P/MPa			x_{C3H6}	P/MPa
0.066 ± 0.002	0.188			0.064 ± 0.002	0.213
0.097 ± 0.002	0.301			0.095 ± 0.002	0.335
0.138 ± 0.003	0.446			0.136 ± 0.003	0.490
0.169 ± 0.004	0.560			0.164 ± 0.004	0.625
0.213 ± 0.005	0.718			0.208 ± 0.005	0.792
0.251 ± 0.005	0.871			0.246 ± 0.005	0.957
0.277 ± 0.005	1.008			0.271 ± 0.006	1.112
0.313 ± 0.006	1.148			0.307 ± 0.006	1.266

[a]The uncertainties of temperature and pressure are ± 0.1 K and ± 0.0016 MPa, respectively.

Table 2. Obtained Experimental Data of Propene Solubility in Heptane[a]

T = 313.4 K		T = 324.8 K		T = 336.2 K	
x_{C3H6}	P/MPa	x_{C3H6}	P/MPa	x_{C3H6}	P/MPa
0.083 ± 0.002	0.136	0.080 ± 0.002	0.166	0.077 ± 0.002	0.201
0.147 ± 0.003	0.239	0.142 ± 0.003	0.284	0.138 ± 0.003	0.334
0.203 ± 0.004	0.342	0.198 ± 0.004	0.402	0.193 ± 0.004	0.467
0.258 ± 0.005	0.431	0.251 ± 0.005	0.511	0.246 ± 0.005	0.591
0.293 ± 0.005	0.546	0.287 ± 0.005	0.630	0.282 ± 0.005	0.721
0.340 ± 0.005	0.636	0.334 ± 0.005	0.733	0.328 ± 0.005	0.841
0.380 ± 0.006	0.739	0.375 ± 0.006	0.845	0.368 ± 0.006	0.963
0.424 ± 0.006	0.845	0.418 ± 0.006	0.972	0.411 ± 0.006	1.107
T = 347.6 K				T = 359.1 K	
x_{C3H6}	P/MPa			x_{C3H6}	P/MPa
0.074 ± 0.002	0.241			0.070 ± 0.002	0.288
0.134 ± 0.003	0.391			0.130 ± 0.003	0.452
0.188 ± 0.004	0.536			0.183 ± 0.004	0.614
0.240 ± 0.005	0.675			0.234 ± 0.005	0.770
0.275 ± 0.005	0.821			0.269 ± 0.005	0.932
0.321 ± 0.006	0.957			0.315 ± 0.006	1.085
0.362 ± 0.006	1.091			0.355 ± 0.006	1.228
0.404 ± 0.006	1.259				

[a]The uncertainties of temperature and pressure are ± 0.1 K and ± 0.0016 MPa, respectively.

$$n_{propene}^{l} = n_{propene} - n_{propene}^{g} \tag{1}$$

$$n_{propene}^{g} = \frac{P_{propene} V_{g}}{Z_{propene} R T} \tag{2}$$

$$x_{propene} = \frac{n_{propene}^{l}}{n_{propene}^{l} + n_{solvent}} \tag{3}$$

where $n_{propene}^{l}$ is the number of moles of the dissolved propene in the liquid solvent, $n_{propene}$ is the number of moles of the injected propene from the injection gas vessel, $n_{propene}^{g}$ is the number of moles of the propene in the vapor phase of equilibrium cell, $P_{propene}$ is the equilibrium partial pressure of propene

obtained by subtracting the vapor pressure of the solvent from the total equilibrium pressure, V_{g} is the volume of the gas phase in the equilibrium cell that is the total volume of the equilibrium cell minus the volume of the liquid phase, $Z_{propene}$ is the compressibility factor of propene calculated using the SRK EOS, R is the gas constant, T is the absolute temperature, and $n_{solvent}$ is the number of moles of the injected solvent.

The reproducibility of the gas solubilities data was estimated by an average value about 1.5 % and about 4 % for maximum deviation by duplication of some experimental runs.

Thermodynamic Modeling. In this work, thermodynamic modeling of the solubility of propene in methylbenzene and heptane was performed using the PR CEOS[11] as:

Table 3. Adjusted Parameters and the AAD % for the Solubility of Propene in Methylbenzene and Heptane

system	parameter	A_1	A_2	AAD%[a]
propene + methylbenzene	k_{ij}	0.3749	−0.0007024	2.10
	l_{ij}	0.01879	−0.0002888	
propene + heptane	k_{ij}	0.9422	−0.002516	1.89
	l_{ij}	0.7390	−0.001980	

[a]AAD % = $100/N \sum (|P_{exp} - P_{cal}|/P_{exp})$.

$$P = \frac{RT}{v - b} - \frac{a}{v^2 + 2bv - b^2} \tag{4}$$

The attractive and repulsive parameters, a and b, of pure components for PR CEOS can be obtained using critical properties as:

$$a = 0.45724 \left(\frac{R^2 T_c^2}{P_c} \right) \alpha(T) \tag{5}$$

$$b = 0.07780 \left(\frac{RT_c}{P_c} \right) \tag{6}$$

$$\alpha(T) = (1 + m(1 - \sqrt{T_r}))^2 \tag{7}$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{8}$$

where T_c, P_c, and ω indicate the critical temperature, critical pressure, and Pitzer acentric factor, respectively. The fluid vdW mixing rule with two adjustable parameters is adopted to express mixture properties as:

$$a_m = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) \tag{9}$$

$$b_m = \sum_i \sum_j x_i x_j \frac{b_i + b_j}{2} (1 - l_{ij}) \tag{10}$$

where a_m and b_m are the attractive and repulsive parameters of mixture, respectively. The $k_{ij} = k_{ji}$ and $l_{ij} = l_{ji}$ are the adjustable parameters can be obtained by correlation of the experimental data. To cover the whole range of temperatures, the k_{ij} and l_{ij} is supposed to vary with temperature linearly as:

$$k_{ij}(\text{or } l_{ij}) = A_1 + A_2 T \tag{11}$$

A_1 and A_2 are constants, and T is the absolute temperature.

■ RESULTS AND DISCUSSION

To validate the experimental setup and the used procedure, the presented methylbenzene solubility data and those obtained by Dariva et al.[1] and Konobeev and Lyapin[6] were compared as shown in Figure 2. According to Figure 2, the presented experimental results show good agreement with those data found by Konobeev and Lyapin.[6] However, the difference between our data and those reported by Dariva et al.[1] can be related to different measuring techniques as they believed; we previously mentioned this in the Introduction section of this paper.

Propene solubilities in methylbenzene and heptane were measured in different pressures and temperatures ranging from (313 to 359) K. Tables 1 and 2 present these experimental solubility data with uncertainty of each data sample. Obviously, the propene solubility in heptane is more than methylbenzene at all experimental conditions. Also it can be found that solubility of
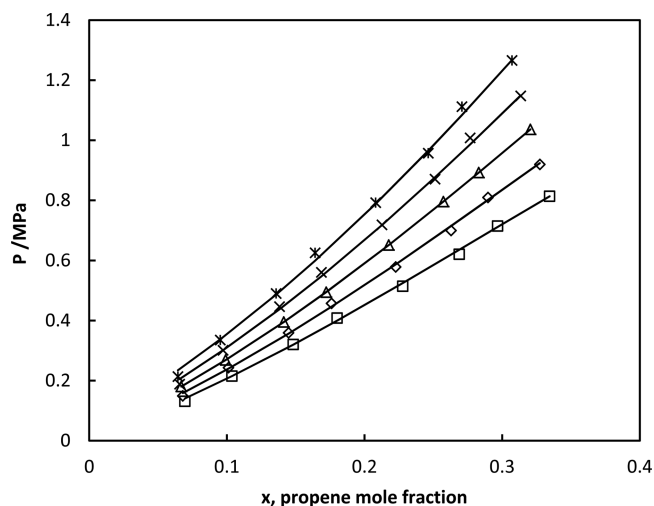
Figure 3. Comparison of calculated bubble pressure using PR CEOS (solid line) and the obtained experimental data (+, T = 359.1 K; ×, T = 347.7 K; △, T = 336.3 K; ◇, T = 324.8 K; □, T = 313.4 K) for the propene + methylbenzene binary system.
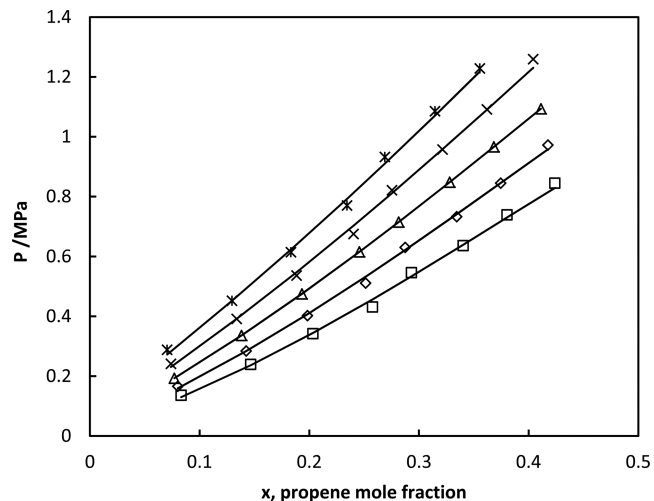
Figure 4. Comparison of calculated bubble pressure using PR CEOS (solid line) and the obtained experimental data (+, T = 359.1 K; ×, T = 347.7 K; △, T = 336.3 K; ◇, T = 324.8 K; □, T = 313.4 K) for the propene + heptane binary system.

propene in both solvents decreases by increasing the temperature.

The experimental data were modeled using PR CEOS with the vdW mixing rule. Table 3 shows the fitted parameters for the presented model and the absolute average deviation percent (AAD %) in calculating the bubble pressures. The values of AAD % confirm the good ability of the PR CEOS with vdW mixing rule for VLE calculation of the studied systems.

Figures 3 and 4 present the comparison of fitted results using Peng−Robinson EOS and the obtained experimental data. It can be observed that the accuracy of the PR CEOS in representing the experimental data is very good.

■ CONCLUSIONS

The accurate amount of dissolved propene gas in various industrial solvents used in slurry-phase propene polymerization is essential to calculate actual polymer productivity and find a

more accurate reaction rate in the early stage of polymerization. For this reason, precise experimental solubility data are needed. The solubilities of propene in methylbenzene and heptane at various propene loadings were measured using a static equilibrium cell over wide ranges of pressure and temperature from (0.13 to 1.27) MPa and (313 to 359) K, respectively. The solubility of propene in both solvents decreases by increasing the temperature. Experimental results show that the propene is more soluble in heptane than methylbenzene by about a 1.2 factor on average. The modeling results show that the PR CEOS with the vdW mixing rule with two adjustable parameters is able to represent the experimental data well.

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Notes
The authors declare no competing financial interest.

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