

Solubility of Ethylene in Toluene and Toluene/Styrene-Butadiene Rubber Solutions

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ABSTRACT: The solubility of ethylene in toluene and in toluene (90 wt %)/styrene-butadiene rubber (SBR; 10 wt %) solutions was determined because the solubility data were of interest for the kinetic study of the metallocene-catalyzed homopolymerization of ethylene and the copolymerization of ethylene with α -olefins. The data were obtained over the temperature range of 293–343 K and the pressure range of 50–180 psi. An original Universal Functional Group Activity Coefficient (UNIFAC) model was applied for the ethylene-

toluene system, and a UNIFAC-ZM model (a modified UNIFAC model proposed by Zhong and Masuoka et al.) was applied for the ethylene-toluene/SBR ternary system. Henry's law was also used to correlate the experimental results of the two systems. A comparison was made between the UNIFAC models and Henry's law. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 645–649, 2005

Key words: rubber; thermodynamics

INTRODUCTION

Olefin polymerization with metallocene-based Ziegler-Natta catalysts has become a subject of great interest since the early 1980s. Many studies have been reported on the kinetics of olefin polymerization with metallocene catalysts, and this is potentially very important for commercial polymerization processes.^{1–3} In the homopolymerization of ethylene and copolymerization of ethylene with α -olefins, the solubility of ethylene is a parameter required to describe the kinetics of the polymerization process in detail.

With respect to organic solvents, toluene has often been used as the reaction medium for the homopolymerization and copolymerization of ethylene.^{4,5} Previous researchers have reported the solubility data of ethylene in toluene at 1, 5, and 10 atm over a temperature range of 268–338 K.⁶ The purpose of this study was to determine the solubility of ethylene in a typical polymerization system to provide fundamental data for kinetic analysis. First, the data of the solubility of ethylene in toluene were measured from 293 K to 343 K at pressures up to 180 psi. These conditions encompassed those commonly encountered in the metallocene-catalyzed homopolymerization of ethylene and the copolymerization of ethylene. The data obtained in this study provide verification of the literature data and further enrich the database. Second, a toluene (90

wt %)/styrene-butadiene rubber (SBR; 10 wt %) solution was used as a model polymerization system; the solubility of ethylene in this solution was measured under the same conditions used for toluene. UNIFAC models and Henry's law were applied to represent the experimental data.

EXPERIMENTAL

Materials

Polymerization-grade ethylene gas was obtained from Praxair, Inc. (Danbury, CT), and was purified by passage through a drying column consisting of 4-Å molecular sieves and a copper oxide catalyst. Analytical-grade toluene was purchased from BDH (Toronto, Canada) and was 99% pure. SBR was obtained from Petrofina, Inc. (Brussels, Belgium) (weight-average molecular weight = 160,000, styrene concentration = 18 wt %).

Apparatus and procedure

A solubility study of ethylene in toluene was carried out in a 300-mL autoclave (Parr Instrument Co., Moline, IL) equipped with a mechanical stirrer, a heater, and a temperature controller. A cooling system was used to accurately control the desired solution temperature to within $\pm 1^\circ\text{C}$. A dip tube (with a 1.59-mm outer diameter) was connected for sampling the equilibrium liquid phase, as shown in Figure 1. The pressure in the reactor was kept constant with an adjustable valve. Toluene (or a toluene/SBR solution; 150 mL) was added to the autoclave. The system was then degassed with three cycles of charging the reactor

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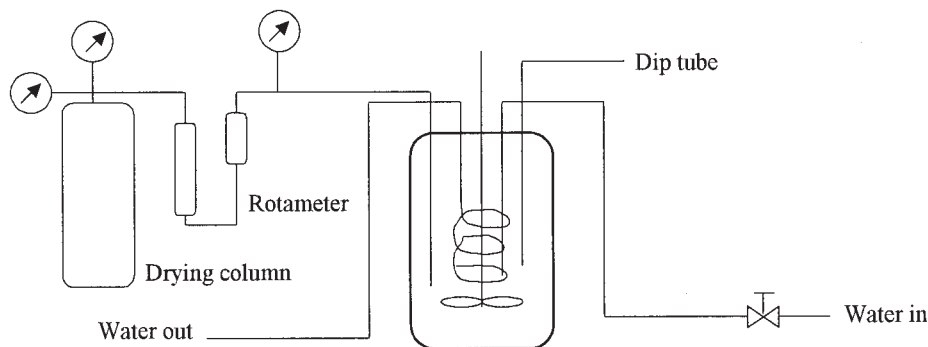


Figure 1 Schematic diagram of the setup for the solubility measurements.

with ethylene gas to 2 atm, allowing the system to equilibrate under vigorous agitation, and releasing the pressure. The reactor was then heated to the desired reaction temperature with agitation at 600 rpm. When the temperature of the autoclave stabilized, ethylene gas was added to the reactor until a designated pressure was reached. According to experimental observations, the equilibrium between the two phases was established for approximately 60 min (30 min for agitation and 30 min for stabilization without agitation). However, the system was maintained for 2 h (1 h for agitation and 1 h for stabilization without agitation) before the sampling to ensure that equilibrium had been established. The results were unaffected by the experimental pressure being approached from above or below.

The analysis technique was based on that previously described in the literature.^{7,8} The samples were withdrawn from the autoclave through a dip tube, which was purged of any vapor. A 60-mL glass tube with a stopcock side arm sealed with an Aldrich (Oakville, Canada) Subaseal rubber stopper was used as a sampling container. When a sample was taken, a slow, continuous flow of the solvent was permitted to purge the dip tube of vapor. Under this flow, the dip tube was inserted through the stopper to inject fluid into the preweighed sample flask. Once it was brought to room temperature, the volume of ethylene that evolved from the sample was determined with a gas burette. The amount of liquid sampled in the procedure was then measured gravimetrically. After accounting for the amounts of ethylene and liquid sampled, we calculated the mass fraction of each component.

MODELING

In this study, original UNIFAC and UNIFAC-ZM (a modified UNIFAC model proposed by Zhong and Masuoka et al.) models were applied to the systems. Henry's law was also used to correlate the experimental results. A comparison was then made of the pre-

diction accuracy of Henry's law and the UNIFAC models.

Original UNIFAC and UNIFAC-ZM models

The UNIFAC model,⁹ which is based on the concept of group contributions, and its modified versions have been widely used to predict liquid-phase activity coefficients (γ_i). The original UNIFAC model has the following form:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (1)$$

where γ_i^C and γ_i^R are the combinatorial and residual parts, respectively. γ_i^C can be obtained as follows:

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} - \frac{\phi_i}{x_i} + 1 - \frac{zq_i}{2} \left[\ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i} \right] \quad (2)$$

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j}, \quad \theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad (3)$$

where x_i is the molar fraction and z is the coordination number (10). q_i and r_i are the volume parameter and surface-area parameter for component i , respectively. γ_i^R can be obtained as follows:

$$\ln \gamma_i^R = \sum_k v_k^i (\ln \Gamma_k - \ln \Gamma_k^i) \quad (4)$$

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \theta_m \Psi_{mk} \right) - \sum_m \frac{\theta_m \Psi_{km}}{\sum_n \theta_n \Psi_{nm}} \right] \quad (5)$$

$$\Psi_{mn} = \exp \left(- \frac{a_{mn}}{T} \right) \quad (6)$$

where Γ_k is the residual activity coefficient of group k in a solution, Γ_k^i is the residual activity coefficient of group k in a reference solution containing only mole-

cules of type i , Q_k is surface-area constant of group k , and v_k^i is the number of k groups in molecule i . Equation (5) also holds for Γ_k^i . θ_m is the surface-area fraction of group m . a_{mn} is the group interaction parameter and can be evaluated from phase equilibrium data.

Generally, the UNIFAC model is a good predictive model for low molecular fluid systems. However, the predicted solvent activities tend to be underestimated when it is applied to polymer solutions. To correct the original UNIFAC model, Oishi and Prausnitz¹⁰ added a Flory free-volume term to the model. Elbro et al.¹¹ combined the combinatorial and free-volume effects and proposed an entropic-FV (free volume) model. However, the two models require accurate molar volumes for both the solvent and polymer, and this limits their applications. In the UNIFAC-ZM model, Zhong et al.¹² proposed a relation between the volume parameters $r(n)$ for n -mer and $r(1)$ for the monomer:

$$r(n) = 0.6538nr(1) \quad (7)$$

They applied it to the combinatorial term modified by Kikic et al.¹³

$$\ln \gamma_i^C = \ln \frac{\phi_i'}{x_i} - \frac{\phi_i'}{x_i} + 1 - \frac{zq_i}{2} \left[\ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i} \right] \quad (8)$$

where ϕ_i' is equal to $\frac{r_i x_i}{\sum_j r_j x_j}$. For the polymer, r is evaluated with eq. (7), whereas in the calculation of ϕ_i with eq. (3), $r(n)$ is equal to $nr(1)$. Therefore, no additional information is needed for this model other than the original UNIFAC group parameters. In this study, the original UNIFAC model was applied to the ethylene-toluene binary system, and the UNIFAC-ZM method was applied to the ethylene-toluene/SBR solution.

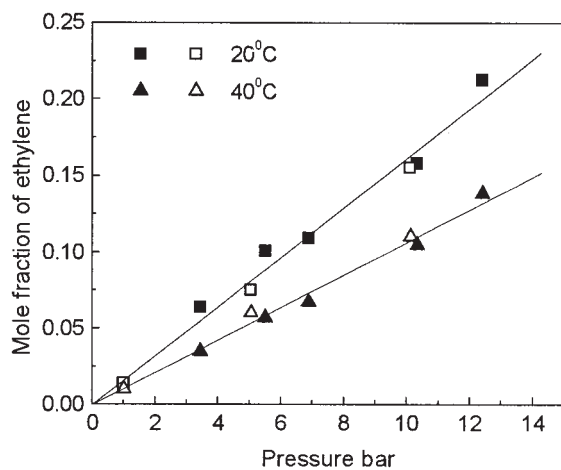


Figure 2 (■,▲) Experimental data versus (□,△) published data (taken from ref. 6).

TABLE I
Solubility of Ethylene in Toluene

Temperature (°C)	Mass fraction				
	50 psi	80 psi	100 psi	150 psi	180 psi
20	0.0202	0.0329	0.0359	0.0539	0.0758
30	0.0156	0.0209	0.0291	0.0453	0.0608
40	0.0108	0.0180	0.0214	0.0343	0.0465
50	0.0083	0.0165	0.0192	0.0307	0.0458
60	0.0072	0.0170	0.0199	0.0253	0.0380
70	0.0070	0.0140	0.0178	0.0260	0.0339

Henry's law

Henry's law has often been used to correlate the solubility of a gas in the liquid phase. It has a very simple form:

$$p = Hm \quad (9)$$

where p is the partial gas pressure, H is Henry's law coefficient, and m is the mass fraction of gas in the liquid phase. Here m was used rather than x_i because the polymer SBR was involved. H depends on the applied temperature.

RESULTS AND DISCUSSION

The solubility measurements in this work were determined with a previously reported analysis technique,⁷ which focuses solely on the composition of the condensed phase. To verify that the experimental method was capable of providing accurate results, we compared these solubility data with published solubility data for ethylene in toluene. Figure 2 illustrates the published points⁶ along with the data collected in our laboratory with the aforementioned procedure. The literature data did not deviate much from the values calculated from a linear regression of our results. This finding agreed with a previous study in which the same technique was used to determine the solubility of hydrogen in chlorobenzene.⁷

After the experimental approach was verified, the solubility of ethylene in toluene and in toluene (90 wt %)/SBR (10 wt %) solutions was then measured over the temperature range of 293–343 K and the pressure range of 50–180 psi. The experimental data are listed in Tables I and II.

The equilibrium for a vapor-liquid system can be expressed as follows:

$$\phi_i y_i p = \gamma_i x_i f_i^0 \quad (10)$$

where ϕ_i is the fugacity coefficient in the vapor phase, y_i is the mole fraction of component i in the vapor phase, and f_i^0 is the pure-component reference fugacity in the liquid state. Under the scope of these experimental conditions, the vapor phase could be consid-

TABLE II
Solubility of Ethylene in Toluene (90wt%)/SBR
(10 wt%) Solutions

Temperature (°C)	Mass fraction				
	50 psi	80 psi	100 psi	150 psi	180 psi
20	0.0142	0.0259	0.0313	0.0452	0.0596
30	0.0118	0.0213	0.0255	0.0411	0.0545
40	0.0119	0.0143	0.0231	0.0322	0.0434
50	0.0093	0.0124	0.0202	0.0247	0.0389
60	0.0063	0.0123	0.0182	0.0253	0.0319
70	0.0054	0.0128	0.0180	0.0259	0.0293

ered an ideal gas; that is, ϕ_i was assumed to be unity. The UNIFAC models were applied to predict γ_i . All the involved volume parameters, surface-area parameters, and group interaction parameters for the UNIFAC models were taken from the literature.⁹ f_i^0 was assumed to be equal to the vapor pressure of the pure component. The vapor pressure of SBR was set to zero, and the vapor pressures of ethylene and toluene were evaluated with the Antoine equation:

$$\ln p = A + \frac{B}{T - C} \quad (11)$$

where p is the pressure (kPa) and T is the temperature (K). For ethylene, A was 13.52, B was 1345.05, and C was 18.31. For toluene, A was 14.01, B was 3100.16, and C was 53.51.¹⁴ Actually, in this study, such a reference liquid state for ethylene was hypothetical because the applied temperature was higher than its critical temperature (282.3 K). Here the reference fugacity for ethylene was calculated by the extrapolation of the vapor pressure of the pure component as a function of temperature into the supercritical region.¹⁵

When Henry's law was applied for the solubility of the gas, H needed to be obtained first. Figure 3 shows

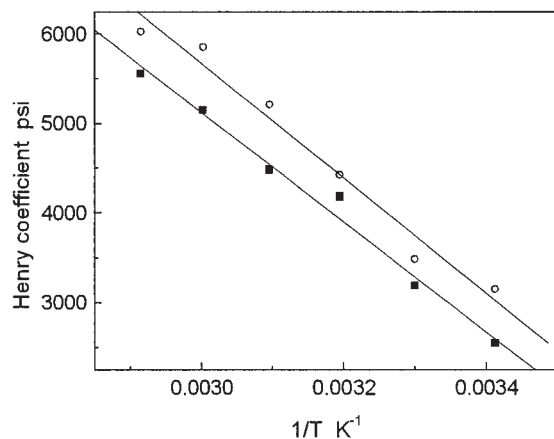


Figure 3 Relationship between H and T in (■) in toluene and (○) in a toluene (10 wt %)/SBR (10 wt %) solution and (—) fitting results with eq. (2).

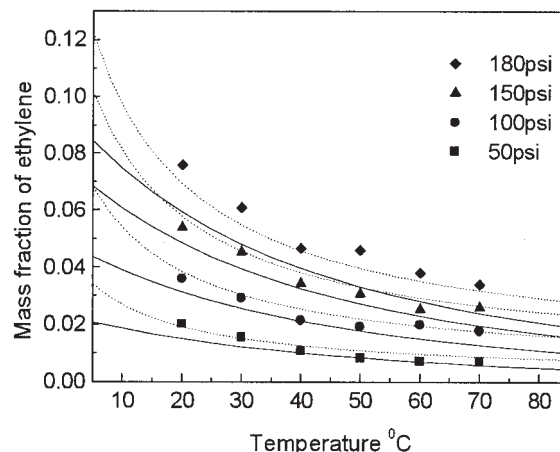


Figure 4 Solubility of ethylene in toluene. The symbols show the experimental data, the solid lines were predicted with the original UNIFAC model, and the dotted lines were calculated with Henry's law.

the temperature dependence of H . The H value at each temperature point was obtained by the fitting of the experimental data with eq. (9). Figure 3 shows that H had a linear relationship with T^{-1} . Therefore, the following expression was used to describe the temperature dependence of H :

$$H = a - b/T \quad (12)$$

where a and b are constants. For the solubility of ethylene in toluene and in toluene (90 wt %)/SBR (10 wt %) solutions, these constants were also regressed with a least-square method. For the ethylene-toluene system, a was 23,484.9, and b was 6,119,600. For the ethylene-toluene (90 wt %)/SBR (10 wt %) system, a was 24,888.8, and b was 6,405,000.

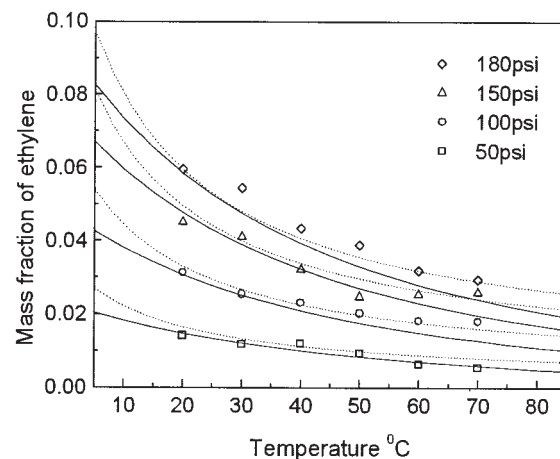


Figure 5 Solubility of ethylene in toluene (90 wt %)/SBR (10 wt %) solutions. The symbols show the experimental data, the solid lines were predicted with the UNIFAC-ZM model, and the dotted lines were calculated with Henry's law.

TABLE III
Comparison of the Predictive Accuracy of the UNIFAC Model, UNIFAC-ZM Model, and Henry's Law

	Ethylene in toluene		Ethylene in toluene (90 wt%)/SBR (10 wt%)	
	AD _{max} %	AAD%	AD _{max} %	AAD%
UNIFAC	30.0	15.6		
UNIFAC-ZM			28.8	10.6
Henry's Law	36.5	10.3	47.7	10.3

m_{exp} : Experimental mass fraction of ethylene; m_{cal} : Calculated mass fraction of ethylene.

$$AD\% = \frac{|m_{exp} - m_{cal}|}{m_{exp}} \times 100\%.$$

$$AAD\% = \frac{1}{n} \sum_{i=1}^n AD_i\%.$$

Figures 4 and 5 show the experimental data and the predicted results from the UNIFAC model and Henry's law. Table III shows the accuracy of the UNIFAC model and Henry's law when they were applied to these systems. The average deviation (AAD%) of the original UNIFAC model was 15.6% when it was applied to the ethylene–toluene binary system, and the average deviation of the UNIFAC-ZM model was 10.6% when it was applied for the ethylene–toluene (90 wt %)/SBR (10 wt %) system. For Henry's law, the deviation was 10.3% for both systems. Although Henry's law had higher precision, there were two param-

eters that were regressed by the experimental data of the objective system. In fact, the UNIFAC models were higher quality because they could be used to predict the solubility without any experiment.

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