Solubility of Ethylene in 2,2,4-Trimethylpentane at Various Temperatures and Pressures

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In this study, the solubilities of ethylene in 2,2,4-trimethylpentane solvent at various temperatures between (323.15 and 423.15) K and pressures between (0.5 and 2.5) MPa were measured by the pressure decay method with vapor composition being analyzed on-line with a gas chromatography. The experimental results show that the solubility of ethylene in 2,2,4-trimethylpentane increases with increasing pressure and decreases with increasing temperature. The experimental data were also expressed in terms of vapor−liquid equilibrium and correlated by the bubble−pressure calculation with the Peng−Robinson equation of state incorporated with the van der Waals one-fluid (vdW-1) and the Zhong−Masuoka (Z-M) mixing rules with the consideration of binary interaction parameters. The results showed the vdW-1 mixing rule is slightly better than the Z-M mixing rule for pressure correlation, but the Z-M mixing rule is slightly better for vapor composition correlation. A semiempirical four-parameter solubility equation in terms of temperature and pressure for the present binary system was proposed. This proposed model is simpler and capable of estimating the solubility with AARD smaller than 5.0 % for the present system.

Introduction

The ethylene−1-octene copolymer is one of the most widely used linear low-density polyethylene (LLDPE). It is a long ethylene polymer with a short side-chain of olefin such as *n*-butylene, *n*-hexene, or *n*-octene as copolymer. The LLDPE has the properties of lower glass transition temperature, high strength, opaque, and good optical property. It can be used as electronic material or photoelectric material. It is a good raw material for producing medical products of conducts, masks, blood bags, and containers due to its hydrophobic property. There are three methods for producing LLDPE by the reaction phase consideration: slurry-phase polymerization, solution-phase polymerization, and gas-phase polymerization. For the solution-phase polymerization, ethylene (the monomer) and 1-octene (the copolymer) are dissolved in the isoparaffin solvent (2,2,4-trimethylpentane) with the presence of metallocene as the catalyst.

It is obvious that the reaction temperature, pressure, and catalyst will affect the properties of LLDPE. But one might think, besides these reaction conditions the concentration of the dissolved ethylene, i.e., the solubility of ethylene, in reaction solution would first decide the extent of polymerization and then the property of LLDPE. Thus, the determination of the solubility of ethylene in the reaction solution is the first step for determining the feasibility of the process and for designing this reaction system. In this study, the solubility of ethylene in 2,2,4-trimethylpentane is the main concern, and that in a 1-octene and 2,2,4-trimethylpentane mixture will be discussed in a different report.

The solubility of a gas in a solvent or solution has been widely studied for a long period. Here, only the works related to the present study are quoted. For instance, Mizan et al.[1] reported that the solubility of ethylene in liquid propylene decreased with increasing temperature in the range of (297 to 333) K, and the solubility data were correlated satisfactorily with the Peng−Robinson equation of state (PR EOS).[2] Li et al.[3] in 1996 reported the solubility of ethylene in *n*-hexane. The same phase behavior was observed by Mizan et al.[1] that the solubility decreased with increasing temperature in the range of (313 to 333) K and pressure range of (0.2 to 5.5) MPa. Gregorowicz[4] studied the solubility of ethylene in tetracosane in the temperature range between (310 and 350) K and pressure up to 11.0 MPa. Lee et al.[5] reported the experimental solubility of ethylene in toluene, norbornene, and cyclic olefin copolymer (COC) mixture at the temperatures of (323.15, 373.15, and 423.15) K and pressure range from (0.5 to 2.5) MPa. The experimental data were satisfactorily correlated with the PR EOS incorporating with the mixing rules of van der Waals and Zhong and Masuok (Z-M).[6] In 2005, Lee et al.[7,8] reported the solubilities of ethylene in pure toluene and in toluene + norbornene mixtures of different compositions. Unfortunately, the experimental data of the present ethylene and 2,2,4-trimethylpentane system have not been reported so far.

Experimental Section

Chemicals. The chemicals used in this study, helium gas (99.99 %) and ethylene (99.5 %) were purchased from Jou-ho Company (Taiwan) and 2,2,4-trimethylpentane (+99.0 %) was the product of Merck Company. All chemicals were used without further purification.

Apparatus and Procedure. In this study, the pressure decaying method was applied to obtain the experimental data since the usual semi-flow and flow methods for high-pressure vapor−liquid equilibrium (VLE) are not suitable to obtain the quantity of gas dissolved in liquid phase. The experimental apparatus and procedure for the present study have been used in our previous work.[5] The apparatus is again schematically shown in Figure 1. Since the descriptions of the apparatus and experimental procedure were given in very detail in our previous work,[5] it will not be repeated here for the reason of brevity of the text. It is worth mention that in this study, the uncertainty

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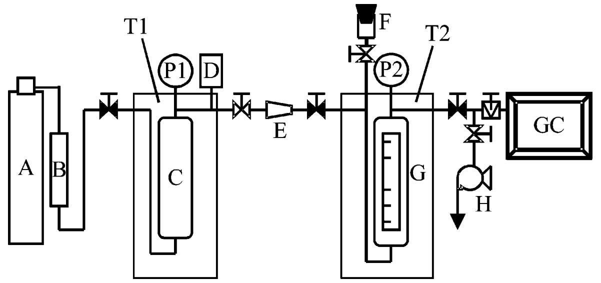

Figure 1. Apparatus for present study: A, high-pressure gas cylinder; B, gas cleaner; C, gas storage tank; D, safety valve; E, single-way valve; F, liquid injector; G, equilibrium cell; GC, gas chromatography; H, vacuum pump; P1 and P2, pressure meter; T1 and T2, temperature meter.

Table 1. Vapor−Liquid Equilibrium of Carbon Dioxide and Toluene System at 352.60 K

	P/kPa	x_{CO2}
ref 9	0.38	0.0200
	1.40	0.0765
	3.08	0.1720
this work	0.28	0.0118
	0.69	0.0333
	1.09	0.0560
	1.61	0.0890
	1.93	0.1092
	2.67	0.1505
	3.03	0.1696

Table 2. Experimental Solubility and VLE Data of Ethylene (1) + 2,2,4-Trimethylpentane (2) System

T	P	solubility × 10^2	liquid phase		vapor phase	
K	MPa	$g_{eth}/g_{2,2,4-tmpt}$	x_1	x_2	y_1	y_2
323.15	0.44	1.532	0.0587	0.9413	0.9429	0.0571
	0.77	2.883	0.1050	0.8950	0.9685	0.0315
	1.30	5.379	0.1797	0.8203	0.9791	0.0209
	1.97	8.874	0.2654	0.7346	0.9866	0.0134
	2.39	10.528	0.3161	0.6839	0.9884	0.0116
373.15	0.68	1.580	0.0604	0.9396	0.8239	0.1761
	1.31	3.407	0.1256	0.8744	0.9068	0.0932
	1.63	4.542	0.1561	0.8439	0.9136	0.0864
	1.97	5.785	0.1906	0.8094	0.9220	0.0780
	2.42	7.635	0.2371	0.7629	0.9316	0.0684
423.15	0.60	0.477	0.0191	0.9809	0.3461	0.6539
	1.20	1.972	0.0757	0.9243	0.6540	0.3460
	1.67	3.137	0.1165	0.8835	0.7361	0.2639
	2.10	4.319	0.1552	0.8448	0.7726	0.2274
	2.32	4.942	0.1747	0.8253	0.7957	0.2043

of solubility measurements is dependent on the uncertainties of weighting the chemicals (± 0.1 mg), of reading the liquid level of equilibrium cell (± 0.01 cm), of temperature indicating (± 0.1 K), of thermostat controlling temperature (± 0.1 K), of reading the pressure (± 0.00069 MPa, ± 1.0 psi), and of other factors. On the basis of the analysis of all the sources of uncertainties, the overall uncertainty of solubility can be determined and illustrated by the significant digits of all experimental data given in Table 2. The detailed procedure of calculation of the overall uncertainty is omitted here for brevity.

Calibration Curves. In this study, three calibration curves were required for the present measurements. To construct the calibration curve of ethylene, the ethylene gas was introduced into the equilibrium cell at constant temperature first and waited for pressure reaching a static value then opened the sampling valve to allow ethylene flow to GC. The volume of ethylene was measured, and the mole number was calculated with the PR EOS[2] with known pressure, temperature, and volume. Then the calibration curve of mole number against peak area was determined. For the calibration curve of 2,2,4-trimethylpentane, a known volume of liquid 2,2,4-trimethylpentane was directly injected into GC. Then the peak area of GC analysis and the mole number, which was estimated with known density at constant temperature, were used to construct the calibration curve. For the calibration curve of ethylene and 2,2,4-trimethylpentane mixture, the standard procedure was used, and the description was omitted here for brevity.

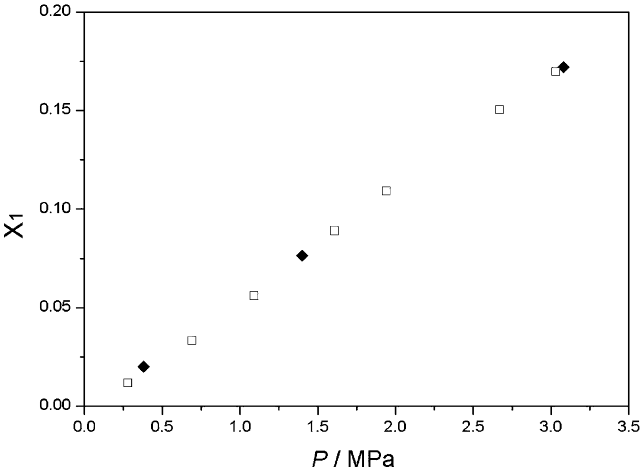

Figure 2. Experimental and literature data of carbon dioxide and toluene system at 352.60 K: □, experimental data; ■, ref 9.

Test Experiment. A test experiment was run on the solubility of carbon dioxide in toluene at 352.60 K before the present experiment to ensure the reliability of the apparatus and experimental skill. The results of this test experiment were compared to the literature data of Ng and Robinson[9] and are given in Table 1. Since there is no match between the present data and the literature data obtained at the same experimental conditions such that the exact comparison between the present data and the literature data can be made. Thus, Figure 2 was drawn to show the good agreement of these two experimental sets.

Ethylene Solubility Calculations

The solubility of ethylene in 2,2,4-trimethylpentane was calculated from the pressure decay in the equilibrium cell and the material balance of ethylene when the gas−liquid equilibrium was reached in the equilibrium cell. The quantity of ethylene flowing from the storage cell to the equilibrium cell, W_{eth} was calculated from the volumetric change of ethylene in the storage cell and expressed by an equation as

$$W_{eth} = MW_{eth} \times \left[\frac{V_s P_{1,I}}{Z_{1,I} R T_{1,I}} - \frac{V_s P_{1,F}}{Z_{1,F} R T_{1,F}}\right] \tag{1}$$

where MW_{eth} is the molecular weight of ethylene; V_s is the volume of the storage cell; $P_{1,I}$ and $P_{1,F}$ are the initial and final pressure of the storage cell, respectively; $T_{1,I}$ and $T_{1,F}$ are the initial and final temperature of the storage cell, respectively. Actually, $T_{1,I}$ and $T_{1,F}$ are identical during experiment. The amount of ethylene flew from the storage cell to the equilibrium cell is equal to the sum of that in vapor phase (W^{v}_{eth}) and in liquid phase ($W_{eth}{}^{l}$) of the equilibrium cell at equilibrium condition:

$$W_{eth} = W^{v}_{eth} + W^{l}_{eth} \tag{2}$$

Since the volume of vapor phase in the equilibrium cell was estimated from the reading of the prescaled side-view glass and

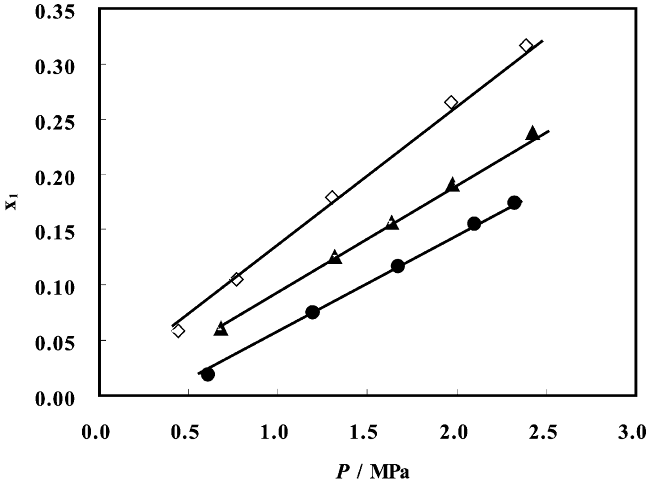

Figure 3. Solubility of ethylene in 2,2,4-trimethylpentane: □, 323.15 K; ▲, 373.15 K; ●, 423.15 K; —, correlation by eq 12.

that of temperature and pressure indicators, then the amount of ethylene in vapor phase can be calculated by

$$W^{\mathrm{v}}_{\mathrm{eth}} = MW_{\mathrm{eth}} \times \left[\frac{V^{\mathrm{v}}P_{2,\mathrm{Feth}}}{Z_{2,\mathrm{F}}RT_{2,\mathrm{F}}}\right] \tag{3}$$

where V^{v} is the volume of vapor phase and $Z_{2,\mathrm{F}}$ is the compressibility factor at the equilibrium conditions $T_{2,\mathrm{F}}$ and $P_{2,\mathrm{F}}$ (partial pressure of ethylene in gas phase). It was calculated by the PR EOS.[2] During our calculation, it is found that the small amount of 2,2,4-trimethylpentane in gas phase at 323.15 K was negligible and will not affect the calculation of the compressibility factor of ethylene. This observation will simplify computation very much. The solubility of ethylene in liquid phase was then calculated by

$$S_{\mathrm{eth}} = \frac{W^{\mathrm{l}}_{\mathrm{eth}}}{W^{\mathrm{l}}_{2,2,4-\mathrm{tmpt}}} \tag{4}$$

and the mole fraction of ethylene in the liquid phase was calculated by

$$x_{\mathrm{eth}} = \frac{W^{\mathrm{l}}_{\mathrm{eth}}/MW_{\mathrm{eth}}}{W^{\mathrm{l}}_{\mathrm{eth}}/MW_{\mathrm{eth}} + W^{\mathrm{l}}_{2,2,4-\mathrm{tmpt}}/MW_{2,2,4-\mathrm{tmpt}}} \tag{5}$$

The mole fraction of 2,2,4-trimethylpentane in the same liquid phase can be calculated in the same way.

Results

The experiments of the present study must be handled with care to prevent any leakage, particularly at higher temperature and pressure conditions. In this study, the solubilities were measured at (323.15, 373.15, and 423.15) K and pressures from (0.47 to 2.89) MPa. To our experience, the present measurement is more difficult than that of vapor−liquid equilibrium with a semi-flow or flow apparatus since it requires a longer time to reach equilibrium. The experimental data were listed in Table 2 and also plotted as Figure 3. It is obviously that the ethylene solubility in 2,2,4-trimethylpentane decreases with increasing temperature and increases linearly with increasing pressure as showed by three isotherms in Figure 3. The solubility data were also represented in terms of the vapor and liquid compositions and plotted in Figures 4 to 6 for (323.15, 373.15, and 423.15) K, respectively. It is obvious that the liquid phase is rich in solvent and vapor phase is rich in ethylene, particularly at lower temperature, 323.15 K, where the content of 2,2,4-trimethylpentane in vapor is negligible.

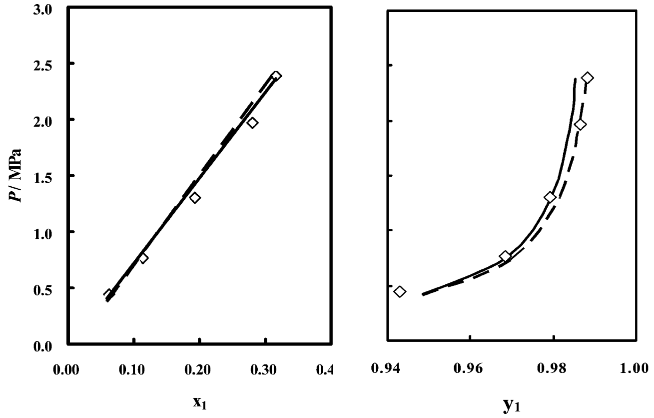

Figure 4. VLE of ethylene (1) + 2,2,4-trimethylpentane (2) binary system at 323.15 K: □, experimental data; —, vdW1 mixing rule ($l_{12} = 0.212$); ---, Z-M mixing rule ($k_{12} = 0.612$).

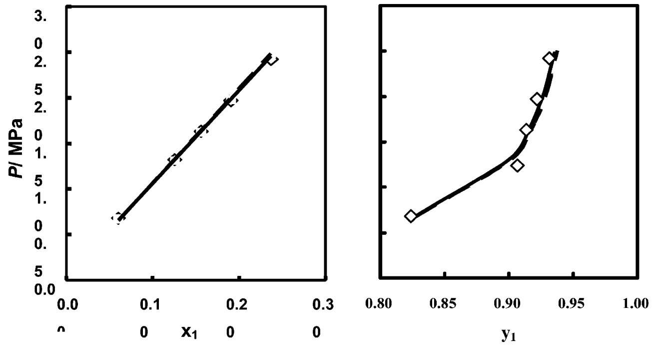

Figure 5. VLE of ethylene (1) + 2,2,4-trimethylpentane (2) binary system at 373.15 K: □, experimental data; —, vdW1 mixing rule ($l_{12} = 0.189$); ---, Z-M mixing rule ($k_{12} = 0.532$)

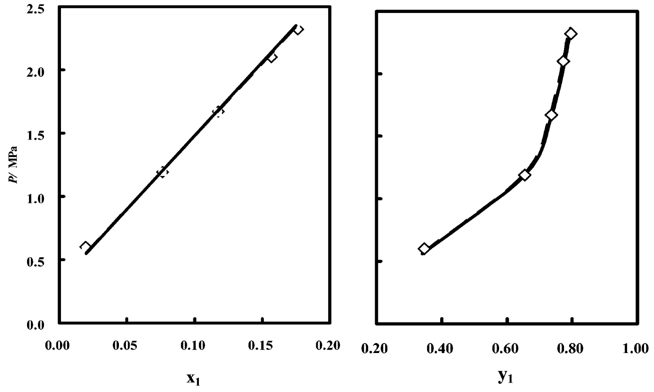

Figure 6. VLE of ethylene (1) + 2,2,4-trimethylpentane (2) binary system at 423.15 K: □, experimental data; —, vdW1 mixing rule ($l_{12} = 0.161$); ---, Z-M mixing rule ($k_{12} = 0.457$)

Reduction of Experimental Data

Empirical Solubility Model with Temperature and Pressure. The solubility of a gas in a liquid depends on the molecule structures and the physical properties of gas and liquid, and the system temperature and pressure. The change of solubility due to the changes of temperature and pressure will be

$$\mathrm{d}K_{\mathrm{eth}} = \left(\frac{\partial K_{\mathrm{eth}}}{\partial P}\right)_{\mathrm{T}} \mathrm{d}P + \left(\frac{\partial K_{\mathrm{eth}}}{\partial T}\right)_{\mathrm{P}} \mathrm{d}T \tag{6}$$

where $(\partial K_{\mathrm{eth}}/\partial P)_{\mathrm{T}}$ and $(\partial K_{\mathrm{eth}}/\partial T)_{\mathrm{P}}$ are the isothermal and isobaric solubility coefficients, respectively. In general, the isothermal coefficients are positive and indicate that the increasing pressure will increase the solubility of gas in liquid. The isobaric coefficient can be positive or negative. A curve with $(\partial K_{\mathrm{eth}}/\partial P)_{\mathrm{T}}$ as vertical axis and temperature as horizontal axis can be plotted from the experimental data. This curve can further be transformed into a straight line if a proper coordinate T^{δ} is selected, for which δ is a parameter to be determined by experimental data. This straight line should be in the formula

$$\left(\frac{\partial K_{\mathrm{eth}}}{\partial P}\right)_{\mathrm{T}} = a_{\mathrm{T}} \times T^{\alpha} + b_{\mathrm{T}} \tag{7}$$

The figure showing $(\partial K_{\mathrm{eth}}/\partial P)_{\mathrm{T}}$ against temperature or against T^{δ} was not difficult to be constructed, and they were omitted here for the reason of the brevity of text. Then the integration of the above equation yields

$$K_{\mathrm{eth}} = a_{\mathrm{T}} \times P \times T^{\alpha} + b_{\mathrm{T}} \times P + c_{\mathrm{T}} \tag{8}$$

With the similar consideration for $(\partial K_{\mathrm{eth}}/\partial P)_{\mathrm{T}}$ and experimental data, three curves showing $(\partial K_{\mathrm{eth}}/\partial T)_{\mathrm{P}}$ versus temperature can be drawn. These three curves can be transformed into three straight lines if the coordinate T^{β} is used instead of T:

$$-\left(\frac{\partial K_{\mathrm{eth}}}{\partial T}\right)_{\mathrm{p}} = a_{\mathrm{p}i}T^{\beta} + b_{\mathrm{p}i} \tag{9}$$

In the above equation, the negative sign was considered since the solubility of ethylene in 2,2,4-trimethylpentane decreases with increasing temperature. Note that parameters $a_{\mathrm{p}i}$ and $b_{\mathrm{p}i}$ are different for different pressures. Equation 9 can further be modified to a form representing all three different pressures with two parameters if P^{γ} is considered instead of P:

$$-\left(\frac{\partial K_{\mathrm{eth}}}{\partial T}\right)_{\mathrm{P}} = a_{\mathrm{p}}P^{\gamma}T^{\beta} + b_{\mathrm{p}} \tag{10}$$

The integration of eq 10 yields

$$K_{\mathrm{eth}} = \frac{-a_{\mathrm{P}}}{\beta + 1} \times P^{\gamma} \times T^{(\beta+1)} - b_{\mathrm{P}} \times T + c_{\mathrm{P}} \tag{11}$$

Equations 8 and 11 should be identical since they represent the same system in this study. Thus, comparing these two equations, one should obtain an equation with four parameters for correlating the experimental solubility of ethylene in 2,2,4-trimethylpentane in this study:

$$K_{\mathrm{eth}} = a_{\mathrm{T}} \times P \times T^{\alpha} + b_{\mathrm{T}} \times P - b_{\mathrm{p}} \times T \tag{12}$$

With this semiempirical solubility equation, the solubilities of ethylene in 2,2,4-trimethylpentane were estimated at the temperatures and pressures of experimental conditions and given in Table 3 with the parameters given at the end of this table. This table showed the largest AARD of this data reduction is 4.82 %.

Phase Equilibrium Correlation

Correlation Model. In this study, the solubility of ethylene in 2,2,4-trimethylpentane is also a problem of gas−liquid equilibrium and the gas solubility data can also be expressed in terms of the gas and liquid compositions through mass balance. Since the system pressure of present study is very high that the phase equilibrium is more properly described by the fugacity coefficient−fugacity coefficient (ø−ø) method. At gas−liquid equilibrium, the temperatures and pressures of two phases are equal and the fugcities of all constituent components in both phases are also equal and expressed by the relation

Table 3. Average Absolute Relative Deviations of Solubility by the PR EOS with the vdW1 and Z-M Mixing Rules and the Proposed Solubility Model for Ethylene in 2,2,4-Trimethylpentane[a]

T	vdW1 mixing rule		Z-M mixing rule		solubility model
K	l_{12}	AARD S %	k_{12}	AARD S %	AARD S %
323.15	0.212	0.17	0.612	0.35	4.79
373.15	0.189	3.70	0.532	3.60	4.19
423.15	0.161	2.86	0.457	2.80	4.82
overall		2.24		2.25	4.60

[a] $K_{\mathrm{eth}} = a_{\mathrm{T}} \times P \times T^{\alpha} + b_{\mathrm{T}} \times P - b_{\mathrm{P}} \times T$; $a_{\mathrm{T}} = 1.750 \times 10^{7}$; $b_{\mathrm{T}} = 1.000 \times 10^{-3}$; $b_{\mathrm{P}} = 2.283 \times 10^{-5}$; $\alpha = -3.844$.

$$y_i\hat{\phi}_i^{v} = x_i\hat{\phi}_i^{l} \quad i = 1, 2, ..., n \tag{13}$$

To obtain the fugacity coefficient, a suitable equation of state is necessary. There are reports related to the present work and are worth mentioning here. Atiqulla et al.[10] compared the results of prediction of the solubilities of ethylene and propylene in toluene by Redlich−Kwang−Soave (RKS) EOS[11] and PR EOS and concluded that the former gave more accurate results than the latter. Mizan et al.[1] correlated their experimental data of the solubility of ethylene in liquid propane with PR EOS. Liu and Wong[12] applied the Schotte EOS[13] with the van der Waals (vdW-1) and the Wong−Sandler (W-S)[14] mixing rules to describe the system of ethylene dissolving in polyethylene and found the former mixing rule provided better results than the latter. Lee et al.[5,7,8] correlated their experimental data of binary, ternary, and quaternary mixtures of ethylene, toluene, norbornene, and COC with PR EOS incorporated with the vdW-1 and M-Z mixing rules fairly well.

After some mathematical manipulations, the fugacity coefficient of component i in a mixture can be obtained (details were not given here) and expressed as

$$\ln \hat{\phi}_i = \frac{b'_{\mathrm{m}}}{b_{\mathrm{m}}}(Z - 1) - \ln(Z - B_{\mathrm{m}}) - \frac{A_{\mathrm{m}}}{2\sqrt{2}B_{\mathrm{m}}}\left[\frac{a'_{\mathrm{m}}}{n}\frac{1}{a_{\mathrm{m}}} - \frac{b'_{\mathrm{m}}}{b_{\mathrm{m}}}\right]\ln\left|\frac{Z + 2.414B_{\mathrm{m}}}{Z - 0.414B_{\mathrm{m}}}\right| \tag{14}$$

where a_{m} and b_{m} were the energy and co-volume parameters of mixture. The other terms in the above equation are as follows:

$$A_{\mathrm{m}} = \frac{a_{\mathrm{m}}P}{(RT)^2}, \quad B_{\mathrm{m}} = \frac{b_{\mathrm{m}}P}{RT}, \quad a'_{\mathrm{m}} = \left[\frac{\partial(n^2 a_{\mathrm{m}})}{\partial n_i}\right]_{T,v,n_{\mathrm{j}\neq\mathrm{i}}}, \quad b'_{\mathrm{m}} = \left[\frac{\partial(n b_{\mathrm{m}})}{\partial n_i}\right]_{T,nv,n_{\mathrm{j}\neq\mathrm{i}}} \tag{15}$$

To estimate the energy and co-volume parameters and the other quantities of a mixture of the above equations, a mixing rule is necessary. The selection of a mixing rule is as important as choosing a suitable EOS. For instance, in this study, the mixing rules of vdW-1 and Z-M were used for our data correlation and are briefly introduced in the Appendix.

Correlation Results. The experimental data given in Table 2 were correlated by the bubble point calculation of the VLE

Table 4. Average Absolute Relative Deviations of Pressure and Gas Composition by the PR EOS with the vdW1 and Z-M Mixing Rules for the Solubility of Ethylene in 2,2,4-Trimethylpentane[a]

T	vdW1 mixing rule			Z-M mixing rule		
K	l_{12}	AARD P %	AAD y $\times 10^2$	k_{12}	AARD P %	AAD y $\times 10^2$
323.15	0.212	1.28	0.94	0.612	3.36	0.87
373.15	0.189	1.19	0.70	0.532	1.36	0.95
423.15	0.161	2.23	0.65	0.457	1.99	0.75

[a] $\text{AAD } P\ \% = \frac{1}{N}\sum \left|\frac{P_{\text{cal}} - P_{\text{exp}}}{P_{\text{exp}}}\right| \times 100\ \%$; $\text{AAD } y = \frac{1}{N}\sum[\sum_i |y_{i,\text{cal}} - y_{i,\text{exp}}|] \times 100\ \%$

consideration. The EOS applied here is PR EOS, and the mixing rules are of the vdW-1 and Z-M.[6] The binary interaction parameters, l_{ij} and k_{ij}, were determined in this correlation step from the objection function:

$$\text{OBJ} = \min\left(\frac{100}{N}\sum_{1}^{N}\left[\frac{|P_{\text{exp}} - P_{\text{cal}}|}{P_{\text{exp}}} + \sum_{i=1}^{k}\left|y_{i,\text{exp}} - y_{i,\text{cal}}\right|\right]\right) \tag{16}$$

where N is the number of data points and k is the number of components.

The correlation results are given in Table 4 showing that the correlation is reasonable by the PR EOS incorporated with the vdW-1 and Z-M mixing rules. This table gives the largest values of AARD of the pressure of 3.36 % at 323.15 K by the Z-M mixing rule and that of gas composition of 0.95 % at 373.15 K by the Z-M mixing rule. For the present system, the vdW-1 mixing rule is slightly better than the Z-M mixing rule as shown by the overall values of AARD. Note that, the binary interaction parameters, l_{ij} and k_{ij}, given in Table 3 were obtained from the correlation of experimental solubility data and those in Table 4 were obtained from the correlation of gas composition. The parameters in these two sets must be identical since the experimental data used for two correlations were from the same phase equilibrium system. The experimental and correlated VLE data of three temperatures were also plotted in Figures 4 to 6. The good agreement of experimental and correlated data is obviously observed from these figures.

Conclusion

With the apparatus set up in our laboratory, the pressure decay method was applied to experimentally determine the solubility of ethylene in 2,2,4-trimethyltentane at temperature between (323.15 and 423.15) K and pressure between (0.5 and 2.5) MPa. The experimental results show that the solubility of ethylene in 2,2,4-trimethyltentane behaves like most other gases in liquid that increases with increasing pressure and decreases with increasing temperature.

A semiempirical equation of temperature and pressure was proposed to represent the experimental solubility of the present system satisfactorily. The experimental data were also correlated by the bubble−pressure calculation of phase equilibrium with the PR EOS incorporated with the vdW-1 and the Z-M mixing rules. The correlation results show the largest values of AARD are of the pressure of 3.36 % at 323.15 K by the Z-M mixing rule and of gas composition of 0.0095 at 373.15 K by the Z-M mixing rule. For the overall consideration of the correlation results of the present system, the vdW-1 mixing rule is slightly better than the Z-M mixing rule as indicated by the values of AARD. In this study, very practical experimental data were provided for developing the process of producing linear low-density polyethylene.

Appendix

In 1996, Zhong and Masuoka considered that at very high pressure the denominator of the repulsive term of a cubic equation of state tends to zero and the contribution of attractive term is much less than the repulsive term and can be neglected. Thus, the excess Helmholtz free energy at high pressure is negligible; Zhong and Masuoka proposed the following mixing rule:[6]

$$a_{\text{m}} = RTQ\frac{D}{1 - D} \tag{A1}$$

$$b_{\text{m}} = \frac{Q}{1 - D} \tag{A2}$$

where D and Q were proposed by Zhong and Masuoka as

$$D = \sum_i z_i \frac{a_i}{b_i RT}; \quad Q = \sum\sum z_i z_j\left(b - \frac{a}{RT}\right)_{ij} \tag{A3}$$

and where

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{\left(b_i - \frac{a_i}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right)}{2}(1 - k_{ij}) \tag{A4}$$

where k_{ij} denotes the binary interaction parameter of the Z-M mixing rule.[6]

The binary interaction parameters l_{ij} and k_{ij} for the vdW-1 mixing rule and the Z-M mixing rule, respectively, were determined in the VLE calculations.

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