Iranian Journal of Chemical Engineering
Vol. 5, No. 4 (Autumn), 2008, IAChE

Predicting Solubility of Isotactic Poly (1-Butene) in Different Organic Solvents by Modified UNIQUAC Model

*H. Salimnezhad and F. Feyzi**

Thermodynamics Research Laboratory, School of Chemical Engineering
Iran University of Science and Technology, Tehran, 16846, Iran.

Abstract

The UNIQUAC activity coefficient model is extended to predict solid-liquid equilibrium of isotactic crystalline poly (1-butene), iPBu-1, in different organic solvents. The UNIQUAC activity coefficient model used in this work is based on the concept of group contribution and consists of combinatorial, residual and free volume terms. To account for branching of atom groups in the monomer structure of the polymer, a correction factor has been applied to the surface parameter of combinatorial and residual terms. Use of this correction factor has significantly improved the accuracy of the model and shows that the proposed activity coefficient model is a proper model for solid-liquid equilibrium calculation in polymer solutions.

Keywords: *UNIQUAC model, Solid-liquid equilibria, IPBu-1, Polymer solutions, Free volume*

Introduction

Understanding solid-liquid equilibria (SLE) in polymer/solvent systems is essential for developing and designing different processes such as: crystallization and fractionation, polymer production, and material development. It is also critical in preventing undesirable fouling of heat exchangers and polymerization reactors. One of the most important thermodynamic factors for the design of these processes is the activity coefficient of the compounds present in the solution. This requires a suitable model capable of predicting the solid-liquid equilibrium conditions.

Since the structure of polymers is complex, the description of SLE in polymer solutions is more difficult than that for vapour-liquid equilibria (VLE) in the same systems. Furthermore, due to their complex nature, experimental measurements of polymer systems are also more difficult and fewer experimental data are available for these systems in literature.

IPBu-1, which was discovered by Natta et al. [1] about 50 years ago, has not been as commercially exploited as other well-known polyolefines like polyethylene or polypropylene. However, high-molecular weight iPBu-1 has found several applications because of its excellent physical properties [2, 3].

The molecular structure of iPBu-1 is illustrated in Fig. 1. It is well known that iPBu-1 exists in several different crystalline forms, which differ in the type of chain

* Corresponding author: E-mail: feyzi@iust.ac.ir

conformation. The high molecular weight of iPBu-1 increases the possible applications of this polymer. IPBu-1 is used in the manufacture of pipes, tubes, pressure sensitive tapes, heavy duty bags, agricultural films, gaskets, and diaphragms. It is also used in the production of house furnishings, electrical apparatus or automotive parts where high impact resistance is needed [2, 3]. Semi crystalline iPBu-1 of lower molecular weight has also been synthesized [4]. This product can be applied as a new additive to gasoline for improving its lubricating properties and lowering its vapor pressure [5]. Domanska et al. [5] and Kozlowska et al. [6- 8] have produced sets of equilibrium data for the SLE of iPBu-1 in different organic solvents in recent years. In this work a thermodynamic model is presented that is able to predict these data accurately.

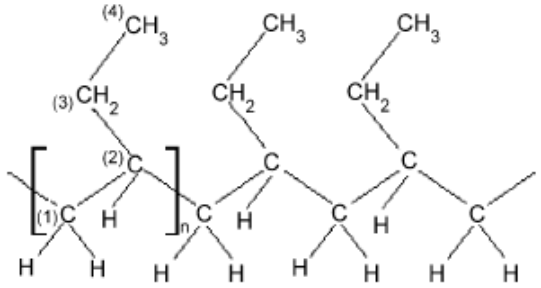

Figure 1. The chemical structure of the iPBu-1 [1]

Thermodynamic framework

For simple eutectic systems, the equality of fugacities of a solid component (1) in liquid (2), neglecting the solubility of the liquid in the solid phase, results in the following equation:

$$x_1 = \frac{f_1^s}{\gamma_1 \, f_1^l} \tag{1}$$

Where x_1 , γ_1, f_1^s and f_1^l are the solubility, activity coefficient, fugacity of the subcooled liquid polymer and the fugacity of the solid polymer, respectively. The ratio of the fugacity of a pure substance in liquid phase to its corresponding value in solid phase is obtained from equation (2) [9].

$$\ln \frac{f_1^l}{f_1^s} = -\ln x_1\gamma_1 = \frac{\Delta_{fus}H_1}{R}\left(\frac{1}{T}-\frac{1}{T_{fus,1}}\right) + \frac{\Delta_{tr}H_1}{R}\left(\frac{1}{T}-\frac{1}{T_{tr,1}}\right) - \frac{\Delta_{fus}C_{p,1}}{R}\left(\ln\frac{T}{T_{fus,1}}+\frac{T_{fus,1}}{T}-1\right) \tag{2}$$

Where $T_{fus,1}$ is the triple point temperature, $\Delta_{fus}H_1$ is the enthalpy of fusion at triple point temperature, $\Delta_{tr}H_1$ is the enthalpy of solid phase transition, $T_{tr,1}$ is the temperature of solid phase transition, $\Delta_{fus}C_{p,1}$ is the difference between the heat capacities of liquid and solid states at the triple point temperature, T is the temperature of the system and R is the universal gas constant.

Calculation of the activity coefficient in the liquid phase requires a suitable thermodynamic model consistent with the configurational properties of the species present in the liquid phase. A suitable thermodynamic model which has been widely used for high molecular weight molecules is UNIQUAC [10]. Since the solute considered in this work is a solid polymer we have taken advantage of this model for evaluating the solubility of the polymer in different solvents. Due to the large size difference between polymer and solvent molecules, it is recommended that an additional term be added to the activity coefficient model which considers the free volume effects [11-16]. The free volume is the volume available to the center of the mass of a single molecule as it moves about the system, while the position of all other molecules remains fixed [15]. In order to obtain more accurate predictions we have

modified the UNIQUAC model by adding a free volume term to it. The model description and the results are presented in the following sections.

The UNIQUAC model and Kannan et al.'s free volume term

The UNIQUAC model was originally developed by Abrams and Prausnitz [10]. It is a generalization of Guggenheim's quasi-chemical theory through the introduction of local area fractions as the primary concentration variable, and the use of Staverman's combinatorial entropy as the boundary condition for athermal mixtures. For a two component system, the activity coefficient based on this model is expressed below:

$$\ln\gamma_1 = \ln\frac{\Phi_1^*}{x_1} + \frac{z}{2}q_1\ln\frac{\theta_1}{\Phi_1^*} + \Phi_2^*\left(l_1 - \frac{r_1}{r_2}l_2\right) - q_1\ln\left(\theta_1 + \theta_2\tau_{21}\right) + \theta_2 q_1\left(\frac{\tau_{21}}{\theta_1+\theta_2\tau_{21}} - \frac{\tau_{12}}{\theta_2+\theta_1\tau_{12}}\right) \quad (3)$$

$$\Phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \quad (4)$$

$$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} \quad (5)$$

$$l_1 = \frac{z}{2}(r_1 - q_1) - (r_1 - 1) \quad (6)$$

$$l_2 = \frac{z}{2}(r_2 - q_2) - (r_2 - 1) \quad (7)$$

Where z is the coordination number which is usually set equal to 10, Φ is the segment fraction and θ is the area fraction. r and q are the volume and surface parameters which are obtained by the UNIFAC group contribution method, and τ_{21} and τ_{12} are the interaction parameters of the model which are obtained from best fit to experimental data through optimization methods.

Kannan et al. [11] proposed a new expression to calculate the free volume contribution to activity coefficient. It was based on generalized van der Waals partition function following Elbro et al. [12] and Flory [13, 14]. The concept behind their new free volume term can be described as follows:

Based on the generalized van der Walls partition function [17], two activity coefficient expressions can be obtained which are introduced below.

The first that accounts for the combinatorial effects together with the free volume effects proposed by Elbro et al. [12] is introduced by equations (8) and (9):

$$\ln\gamma_i^{c+fv} = \ln\left[\frac{\varphi_i^{fv}}{x_i}\right] + 1 - \left[\frac{\varphi_i^{fv}}{x_i}\right] \quad (8)$$

$$\varphi_i^{fv} = \frac{x_i\left(v_i - v_i^*\right)}{\sum_j x_j\left(v_j - v_j^*\right)} \quad (9)$$

Where x_i is the mole fraction, v_i, is the molar volume and v_i^* is the molar hardcore volume of component i, respectively. There are different ways to calculate the molar hardcore volume. In this work, the values of Bondi [18] have been used.

The second expression for the activity coefficient which is derived from Flory-Huggin's combinatorial term by Elbro et al. [12], accounts for the combinatorial effects alone and is as seen below:

$$\ln\gamma_i^c = \ln\left[\frac{\varphi_i^h}{x_i}\right] + 1 - \left[\frac{\varphi_i^h}{x_i}\right] \quad (10)$$

$$\varphi_i^h = \frac{x_i v_i^*}{\sum_j x_j v_i^*} \quad (11)$$

Kannan et al. [11] obtained their new free volume contribution by subtracting equation

(10) from equation (8). The result is a new expression which accounts for the free volume term alone:

$$\ln \gamma_i^{fv} = \ln\left[\frac{\varphi_i^{fv}}{\varphi_i^{h}}\right] + \left[\frac{\varphi_i^{h} - \varphi_i^{fv}}{x_i}\right] \qquad (12)$$

Equation (12) has been used in this work to consider the free volume effects in the SLE calculations of polymer solutions.

Modelling the solubility of solid iPBu-1 in organic solvents

The UNIQUAC model is predictive for normal fluid mixtures in VLE and liquid-liquid equilibria (LLE) calculations. But its applicability for SLE calculations of polymer solutions should be the aim of research [10]. In order to improve the accuracy of the UNIQUAC model for iPBu-1 solutions, a free volume term, described in the previous section, has been added to it. The activity coefficient of component 1 is obtained from equation (13) in which γ_1^c, γ_1^r and γ_1^{fv} are the contributions to the activity coefficient due to the combinatorial, residual and free volume effects, respectively.

$$\ln \gamma_1 = \ln \gamma_1^c + \ln \gamma_1^r + \ln \gamma_1^{fv} \qquad (13)$$

By substitution of the combinatorial and residual terms from the UNIQUAC model [10] and the Kannan et al. free volume expression [11] into equation (13), the following equation is obtained.

$$\begin{aligned}\ln \gamma_1 = {} & \ln \frac{\Phi_1^*}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_1}{\Phi_1^*} + \Phi_2^* \left(l_1 - \frac{r_1}{r_2} l_2 \right) \\ & - q_1 \ln \left(\theta_1 + \theta_2 \tau_{21} \right) \\ & + \theta_2 q_1 \left(\frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} - \frac{\tau_{12}}{\theta_2 + \theta_1 \tau_{12}} \right) \\ & + \ln \left(\frac{\varphi_1^{fv}}{\varphi_1^{h}} \right) + \left(\frac{\varphi_1^{h} - \varphi_1^{fv}}{x_1} \right)\end{aligned} \qquad (14)$$

Considering the calculation of the surface parameter in the UNIQUAC model, the atom's stereo array in the molecule of the monomer is not considered and only the existing functional groups are taken into account. Therefore, the effects of the difference in the atom's stereo array on the behavior of the solution and the activity coefficient of the molecules are ignored.

As shown in Fig. 1, there are four carbon atoms and functional groups in the iPBu-1 monomer. Only two of them are in the main chain of the polymer and the other two atoms are standing as the side chain. Since any change in the atom's stereo array or in the molecule conformation affects the surface area of the molecule, they should be considered in the calculation of the surface area. In this work, in order to consider these effects in the calculation of the activity coefficient, a correction factor has been applied to the surface parameter of the UNIQUAC model. This correction factor has been assigned through mathematical optimization calculations, and its value is set equal to 0.923. Finally, the applied parameters in the proposed activity coefficient model, eq. (14), are:

$$r_i = \sum_k v_k^{(i)} R_k \qquad (15)$$

$$q_i = 0.923 \left(\sum_k v_k^{(i)} Q_k \right) \qquad (16)$$

Where R_k and Q_k are the relative volume and relative surface area parameter contributions of each group and $v_k^{(i)}$ is the number of group k in molecule i.

The activity coefficient model of equation (14) has two adjustable parameters in its residual term, representative of binary interactions between polymer and solvent molecules. In this work, these parameters have been adjusted to experimental solubility data using the genetic algorithm optimization procedure. The objective function (OF) to be

minimized in the optimization procedure is as follows:

$$OF = \frac{\sum_{i=1}^{N} \left| x_{i\,\exp} - x_{i\,\mathrm{cal}} \right|}{N} \quad (17)$$

N is the number of experimental points for each polymer-solvent system for which the data is obtained from references [4-7]. Considering the Gibbs-Duhem equation and following the same procedure introduced in reference [9], an optimum average value for interaction parameters (τ_{ij}) is obtained over the whole range of temperatures of experiments for each system under consideration. This optimum value is then used to calculate the solubility of the solid polymer in solvent.

Results and Discussion

The modified UNIQUAC activity coefficient model has been applied to 14 binary solvent + iPBu-1 systems including 246 data points [4-7]. Tables 1 and 2 show physical properties for high molecular weight and low molecular weight iPBu-1. All of the properties of polymers in Tables 1 and 2 have been obtained experimentally by Kozlowska et al. [7]. Molecular weight and molar volume for different organic solvents used in this work are presented in Table 3.

Using the proposed modification, SLE calculations have been performed to calculate the solubility of iPBu-1 in different organic solvents by equations 1 and 2. The total average absolute deviation of the iPBu-1 mole fraction in 14 different binary polymer solutions was 20.54% for the original UNIQUAC model (Model A) without a free volume term versus 17.01% for the UNIQUAC-FV model with Kannan et al.'s free volume term [11] (Model B), and 15.31% for the corrected model proposed in this work (Model C). The absolute error and number of data points for each solvent + iPBu-1 system is presented in Table 4. It is obvious in this table that the mean average absolute error is decreased going from model A to model C.

Table 1. Molecular characteristics of iPBu-1 [7]

polymer	M_n	M_w	M_w/M_n
High molecular weight iPBu-1	18708	35102	1.876
Low molecular weight iPBu-1	16812	30682	1.83

M_n: number average molecular weight, M_w: weight average molecular weight, M_w/M_n: polydispersity of polymer

Table 2. Physical properties of iPBu-1 [7]

Polymer	T_{fus}(K)	Δ_{fus} H (J/mol)	$V_m^{298.15}$ (cm^3/mol)	T_{tr}(K)	Δ_{tr}H (J/mol)
High molecular weight iPBu-1	376.83	4348.78	49.13	349.60	2451.90
Low molecular weight iPBu-1	383.93	4535.17	49.27	350.65	2361.51

Table 3. Molecular weight and molar volume of different organic solvents [4-7]

Solvent	Molecular Weight (g/mol)	$V_m^{298.15}$ (cm^3/mol)
2,2-Dimethylbutane	86.18	133.72
3-Methylpentane	86.18	130.62
Cyclodecane	140.27	163.9
Cycloheptane	98.19	121.7
Cyclooctane	112.22	134.83
n-Decane	142.29	195.95
n-Octane	114.23	163.51
n-Octadecane	245.50	326.5
Toluene	92.14	106.89
n-Tridecane	184.37	244.9

Table 4. Average absolute percent deviation (AAD%) for different systems and different activity coefficient models, and mean average absolute error

No.	System	Model A Error*	Model B Error*	Model C Error*	Temperature range, K	Reference
1	iPBu-1 & 2,2-Dimethylbutane	17.78	18.35	14.04	303.7-314.6	[6]
2	iPBu-1 & 3-Methylpentane	17.07	14.74	17.54	291.8-318.3	[6]
3	iPBu-1 & Cyclodecane	24.15	17.07	11.88	317.7-362.2	[6]
4	iPBu-1 & Cycloheptane	8.78	6.04	6.49	306.5-353.6	[4]
5	iPBu-1 & Cyclooctane	9.23	17.71	13.38	316.4-357.1	[4]
6	iPBu-1 & n-Decane	25.08	22.79	17.99	308.3-351.8	[7]
7	iPBu-1 & n-Octane	22.06	19.66	19.93	304.5-331.4	[7]
8	iPBu-1 & n-Octadecane	33.55	13.21	14.78	309.9-362.4	[6]
9	iPBU-1 & Toluene	21.19	20.08	19.37	314-351.6	[6]
10	iPBu-1 & n-Tridecane	12.88	16.04	13.55	284.7-358.7	[5]
11	LMW iPBu 1 & 3-Methylpentane	28.09	29.89	23.27	293.2-300.3	[6]
12	LMW iPBu 1 & Cyclodecane	5.59	5.49	5.46	316.2-340.7	[6]
13	LMW iPBu 1 & n-Octadecane	21.61	18.89	19.79	310.2-358.3	[6]
14	LMW iPBu 1 & Toluene	21.18	18.09	17.69	317.4-346.4	[6]
	Mean Average Absolute Deviation	20.54	17.01	15.31		

* The deviation related to models A, B and C is the AAD% for the corresponding data points defined as: $\frac{1}{N}(\Sigma\left|\frac{\text{experimental}-\text{calculated}}{\text{experimental}}\right|)\times 100$

In Tables (5-7) the interaction parameters of Models A, B and C which are obtained by the best fit of experimental data using the genetic algorithm procedure is presented.

Table 5. The values of the interaction parameters of the model C for different polymer-solvent systems

Polymer (1)	Solvent (2)	τ_{12}	τ_{21}
High molecular weight iPBu-1	2,2-Dimethylbutane	0.60254	1.7073
	3-Methylpentane	0.08948	2.84841
	Cyclodecane	0.20258	2.42411
	Cycloheptane	0.21238	2.42868
	Cyclooctane	0.22382	2.37918
	n-Decane	0.22537	2.44966
	n-Octane	0.29992	2.2491
	n-Octadecane	0.16639	2.53439
	Toluene	0.19014	2.40966
	n-Tridecane	0.12775	2.73883
Low molecular weight iPBu-1	3-Methylpentane	0.47316	2.11346
	Cyclodecane	0.42246	2.00897
	n-Octadecane	0.24105	2.39518
	Toluene	0.6994	1.4298

Table 6. The values of the interaction parameters of the model A for different polymer-solvent systems

Polymer (1)	Solvent (2)	τ_{12}	τ_{21}
High molecular weight iPBu-1	2,2-Dimethylbutane	0.66587	1.21616
	3-Methylpentane	0.32711	1.72491
	Cyclodecane	0.27017	1.98832
	Cycloheptane	0.29419	1.84025
	Cyclooctane	0.29464	1.87977
	n-Decane	0.36853	1.80155
	n-Octane	0.50012	1.50152
	n-Octadecane	0.32649	1.92067
	Toluene	0.13457	2.25617
	n-Tridecane	0.21513	2.25721
Low molecular weight iPBu-1	3-Methylpentane	0.95402	1.00053
	Cyclodecane	0.57755	1.49586
	n-Octadecane	0.3176	2.0277
	Toluene	0.47508	1.5396

Table 7. The values of the interaction parameters of the model B for different polymer-solvent systems

Polymer (1)	Solvent (2)	τ_{12}	τ_{21}
High molecular weight iPBu-1	2,2-Dimethylbutane	0.63962	1.56342
	3-Methylpentane	0.22257	2.3704
	Cyclodecane	0.2287	2.32616
	Cycloheptane	0.24577	2.31015
	Cyclooctane	0.25053	2.28231
	n-Decane	0.31158	2.16364
	n-Octane	0.94074	1.13478
	n-Octadecane	0.00672	3.13084
	Toluene	0.20264	2.38771
	n-Tridecane	0.17596	2.53038
Low molecular weight iPBu-1	3-Methylpentane	0.51032	1.95957
	Cyclodecane	0.61799	1.61814
	n-Octadecane	0.28921	2.22564
	Toluene	0.69276	1.44352

Comparing the values of the parameters of models A, B, and C shows that the order of magnitude of their values is the same in the three models. In all cases the value of the parameter τ_{21} is higher than the value of parameter τ_{12} and only slight differences in their values are observed. It can be concluded that the physical significance of the parameters have been saved by applying different modifications to the UNIQUAC model. The better results of model C are due to the more realistic and more meaningful modifications made to the original UNIQUAC model developed in this work.

In Figs. 2 and 3 the prediction of the model for the solubility of solid iPBu-1 in two organic solvents is presented. The solubility of solid iPBu-1 in cycloheptane is shown in Fig. 2, and Fig. 3 illustrates an example of the calculated phase diagram for low molecular weight iPBu-1 in cyclodecane. Very accurate prediction of the model is observed in these figures.

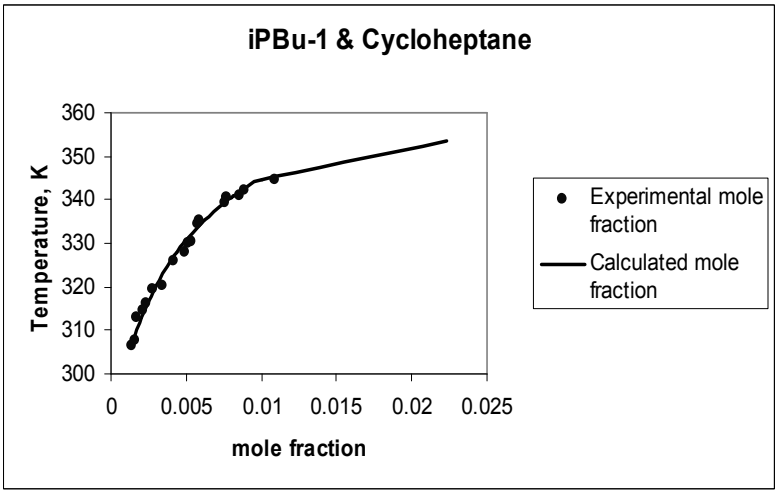

Figure 2. T-x phase diagram for solubility of solid iPBu-1 in cycloheptane expermental data from [4]

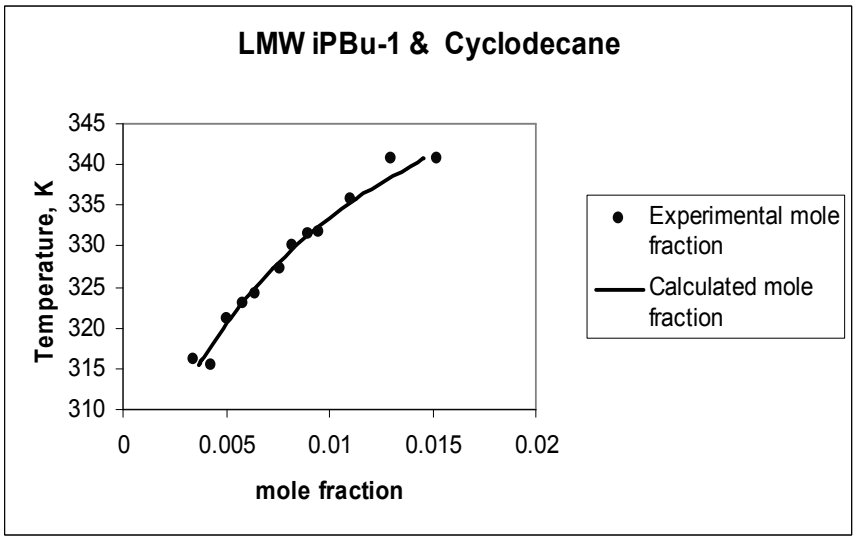

Figure 3. T-x phase diagram for solubility of solid LMW iPBu-1 in cyclodecane expermental data from [6]

Using this model in SLE calculations, we also compared the solubility behaviour of iPBu-1 in different organic solvents. For example, Domanska et al. [4-6] and Kozlowska et al. [7, 8] showed that the solubility of low molecular weight iPBu-1 is more than the solubility of high molecular weight iPBu-1 in the same solvent at the same temperature. It is observed in Fig. 4 that as the molecular weight of the polymer increases, the solubility of the polymer in the same solvent decreases. This result indicates that the same behavior is predicted correctly using the proposed model.

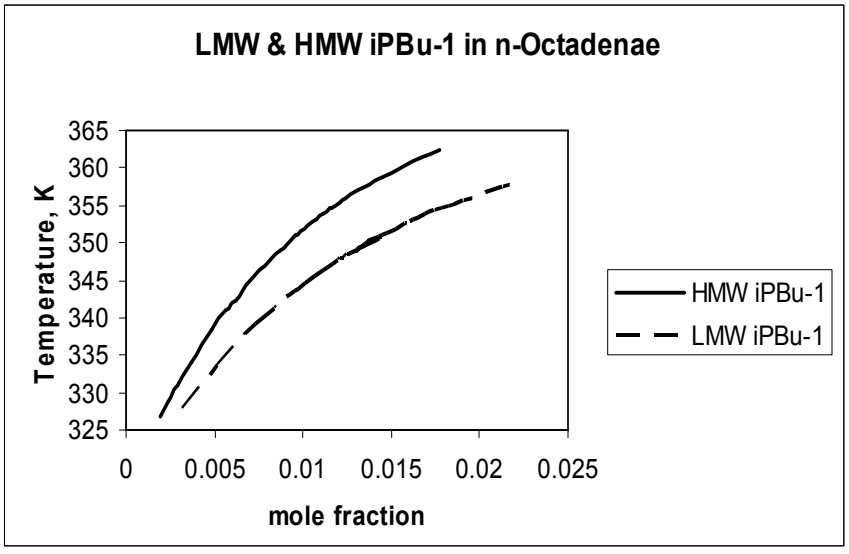

Figure 4. Comparison between the solubility of HMW and LMW iPBu-1 in n-Octadecane

Conclusions

The solubility of solid isotactic crystalline poly (1-butene) in different organic solvents is calculated in this work by modification of the UNIQUAC model. The modification includes the addition of a free volume term which corrects the model for the effects of large differences between the size of the polymer and solvent.

Besides the addition of a free volume term to the UNIQUAC model, the surface parameter of the polymer molecule is also corrected. Using the modified UNIQUAC model in SLE calculations, the experimental results obtained by Domanska et al. [4, 5] and Kozlowska et al. [6-8] for the solubility of solid iPBu-1 in different organic solvents are predicted with reasonable accuracy. The model prediction for the effect of molecular weight on the solubility of iPBu-1 in different organic solvents is also accurate and reliable.

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