SOLVENT ACTIVITY COEFFICIENTS AT INFINITE DILUTION IN POLYSTYRENE-HYDROCARBON SYSTEMS FROM INVERSE GAS CHROMATOGRAPHY

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Abstract—Inverse gas chromatography was used to measure activity coefficients of solvents at infinite dilution over a temperature range from 373.15 K to 423.15 K for monodisperse polystyrene-hydrocarbon systems. Polystyrene has average molecular weight $2.89 \times 10^5$. Solvents include six aliphatic hydrocarbons such as cyclohexane, methyl ethyl ketone, n-hexane, carbon tetrachloride, acetonitrile and acetone and three aromatic ones as benzene, toluene and p-xylene. The measured data of activity coefficients of solvents were predicted by UNIFAC-FV model. We, also, presented a modified UNIFAC-FV model by empirically assigning to it a temperature-dependent C parameter in the free volume contribution of the model. Fitted results demonstrated that the modification of the model fitted the experiments better than the original one.

Key words: Inverse Gas Chromatography, Vapor-liquid Equilibria, Activity Coefficient, Modified UNIFAC-FV, External Degree of Freedom

INTRODUCTION

In design and operation of various polymer processing such as recovery of solvents, polymerization, manufacture of polymer films, fluid-phase equilibria of polymer solutions are required. Measurements of vapor-liquid equilibria (VLE) for polymer solutions were originated in 1930's and they have been accelerated in accordance with a progress of new synthetic polymers and rubbery materials. The measurement [Merk et al., 1980; Grater et al., 1984; Roth and Novak, 1986] of phase behavior for the polymer solution systems which consisted of volatile solvent-non-volatile solute (polymer) generally has performed by inverse gas chromatography (IGC) method. The method required a short time for arriving at VLE and produced the reliable data and was convenient to use. This method is an indirect method which can afford to determine the desirable thermodynamic properties from the experimental data and has been used by many researchers. The data reduction equations representatively were proposed by Conder and Purnell [1968a; 1968b; 1969a; 1969b] and have been used extensively since the Smidsrod and Guillet [1969] first used the method. On the other hand, the polymer solution models that could predict or correlate with the thermodynamic properties obtained by the reduction equations for polymer solution systems have been developed variously. Oishi and Prausnitz [1978], Holten-Anderson et al. [1987], Iwai et al. [1985] and Iwai and Arai [1989] proposed the group contribution models for predicting VLE of polymer solution systems and Bonner and Prausnitz [1973], Chen et al. [1990], Chen [1993], and Choi et al. [1995] also presented the correlative models for their polymer solution systems.

In this work, the activity coefficients of the solvents based on the weight fraction at infinite dilution are measured by the IGC method for solvent(1)/polymer(2) systems at 373.15 K, 393.15 K, 423.15 K. The polymer is polystyrene and the solvents are aliphatic hydrocarbons (cyclohexane, methyl ethyl ketone, n-hexane, carbon tetrachloride, acetonitrile, acetone) and aromatic hydrocarbons (benzene, toluene, p-xylene). Besides the UNIFAC-FV model proposed by Oishi and Prausnitz [1978] to predict VLE of polymer solution systems will be modified to calculate VLE of polymer solutions at infinite dilution. Activity coefficients of solvents at infinite dilution will be calculated, and they will be compared with the experimental data.

EXPERIMENTAL

1. Reagent

All solvents such as the aliphatic hydrocarbons (cyclohexane, methyl ethyl ketone, n-hexane, carbon tetrachloride, acetonitrile, acetone) and the aromatic hydrocarbons (benzene, toluene, p-xylene) were used as special grade obtained from Wako Pure Chemicals, Ltd. And they were used without further purification. The polystyrene as the polymer was a monodisperse polymer ($M_n = 2.89 \times 10^5$, $M_n/M_w = 1.86$) obtained from Pressure Chemicals, Ltd. (USA).

2. Column Preparation

A column preparation should be proceeded to obtain VLE data for the polymer solution systems by IGC method. The column preparation is carried out by next procedure: the weighed polystyrene ($m_p$) is dissolved in the solvent (tetrahydrofuran), and the weighed solid support (fluoropak-80 60/80 mesh) to be used regardless of the sample size or the polarity of solvents is put into the dissolved solution. And then mixture is heated slightly and slowly stirred to eliminate some residue of solvent and cooled to room temperature and completely dried in vacuum dry oven throughout the night. The column preparation is completely carried out by packing the coated material into a stainless steel column (2 m, ID 3 mm). The coating ratio (weight of polymer/weight of solid support) of packing material was 8.53% in this work.

3. Apparatus and Method

The VLE apparatus used for measuring VLE in this work is

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similar to those of Chang and Bonner [1975], Newman and Proussnitz [1972], Iwai et al. [1985] and is shown in Fig. 1. As shown in Fig. 1, the apparatus consists of the parts of carrier gas, IGC, flow rate, and measurement of pressure between inlet and outlet of the column. The inverse gas chromatograph was a Shimadzu GC-3BTD equipped with a thermal conductivity detector. The pressures of carrier gas (He gas) and those of inlet and outlet of the column were measured by the precision pressure gauge and the mercury manometer respectively. The precision pressure gauge was a Nagano Keiki Seisakujo GP20-241.

On the other hand, to measure VLE for the solvent (polymer) systems at infinite dilution, the packed column was equipped into IGC and two needle valves (No. ~) of apparatus shown in Fig. 1 were closed and valve (2) was opened so that the carrier gas was flowed continuously into IGC body during a given period of time. VLE in the column could be identified by keeping a constant baseline of the recorder at the experimental temperature. The flow rate \(Q_{\text{He}}\) of carrier gas was measured by the bubble flow meter at the room temperature and the atmospheric pressure. Then a very small amount (0.1 \(\mu\)) of solvent with air was injected into the column by the microsyringe after the constant baseline of the recorder was identified to prove the VLE of polymer solution in the column.

At that time, the retention times of the air and the solvent were read from the recorder respectively and the pressures of the inlet \(P_i\) and the outlet \(P_o\) of column were measured by the mercury manometer after reading of retention times. All of data which were observed above were put into the following equation of Conder and Purnell [1968a; 1969a; 1969b].

\[
V_i = \frac{273.15 \nu_i}{\rho_i - \rho_{\text{pol}} - \rho_{\text{pol}}} P_i - P_{\text{pol}} \frac{273.15 \nu_i}{T_m}
\]  
(1)

Therefore the specific retention volumes \(V_i\) according to changes of the flow rate \(Q_{\text{He}}\) of carrier gas were obtained from Eq. (1) and plotted on Figs. 2 to 4. The specific retention volumes \(V_i\) at infinite dilution could also be obtained from Figs. 2 to 4 by extrapolation method. In Eq. (1), \(J_i^2\) known as James-Martin factor means a pressure correction factor for the pressure between inlet and outlet of the column and is represented by Eq. (2).

\[
J_i^2 = 3 \left( \frac{P_i}{P_o} \right)^2 - 1
\]
\[
2 \left( \frac{P_i}{P_o} \right)^3 - 1
\]  
(2)

To obtain the activity coefficients of solvent at infinite dilution, the specific retention volumes \(V_i\) at infinite dilution obtained from Figs. 2 to 4 finally were substituted into the following Patterson's equation [1969].

\[
\Omega = \left( \frac{a_i}{w_i} \right)^2 = \frac{273.15 R}{P_i V_i M_i} \exp \left[ -\frac{P_i}{RT} (B_i - v_i) \right]
\]  
(3)

Therefore the infinite dilution activity coefficients \(\Omega\) of sol-