

PREDICTION OF ACTIVITIES OF SOLVENTS IN CONCENTRATED COPOLYMER SOLUTIONS

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Abstract – A gas chromatographic method was used to measure the activities of solvents for solvent/poly(vinylchloride : vinylacetate=88 : 12, wt%) systems in the temperature range from 398.15 K to 438.15 K. The solvents were n-octane, benzene, ethylbenzene, chlorobenzene and p-xylene. The UNIFAC and the ASOG models were revised to predict the activities of solvents in concentrated copolymer solutions. They were designated as UNIFAC-FA (UNIFAC Free volume and Attraction) and ASOG-FA (ASOG Free volume and Attraction), respectively. The activities of solvents were predicted with their models for solvent/poly(vinylchloride : vinylacetate=88 : 12, wt%) systems. The values predicted by each model were compared with the experimental data.

Key words: Gas Chromatographic Method, Copolymer Solution, Activities of Solvents, UNIFAC, ASOG

INTRODUCTION

Copolymers are commercially superior to homopolymers from the point of view of mechanical properties (optical properties, shock intensity, manufacturing, adhesive strength) and chemical ones (proof-chemicals, thermal stability). The research into the phase behavior of copolymer mixtures has been scarcer than that of homopolymer mixtures in spite of much industrial interest. The useful properties of various copolymers are derived from the fact that the polymer chain is copolymerized with functional groups more than is one kind of monomer.

Experimental measurements and thermodynamic presentations of copolymer solutions are more scarce because of the heterogeneous properties of copolymers. Though the thermodynamic properties of the copolymer solutions are important, industries have not shown much interest in the field of phase equilibria or thermodynamic interpretation because the phase behaviors of copolymer solutions are complex and unpredictable. For these reasons, the thermodynamic study of copolymer solutions has proceeded slowly.

A few researchers have, however, attempted to measure the vapor-liquid equilibria (VLE) for copolymer solutions or proposed models to predict or correlate the thermodynamic properties of mixtures containing copolymers. Among the various methods to measure VLE of polymer solutions, a gas chromatographic method has generally been used because it takes only a short time to reach VLE. The method has been improved by Bonner and Brockmeier [1977] since Smidsord and Guillet [1969] used it at the beginning. On the other hand, much research on thermodynamic calculation for polymer solutions has been performed by using predictive and correlative ap-

proaches. Oishi and Prausnitz [1978] suggested the UNIFAC-FV to predict the VLE for various polymer solutions by adding a free volume term to the UNIFAC model [Fredenslund et al., 1977]. Choi et al. [1995] also suggested the ASOG-FV by adding modified free volume terms to the ASOG model [Tochigi et al., 1990] for calculating the activities of solvents in concentrated homopolymer solutions. And Choi et al. [1996] and Kim et al. [1996] reported experimental infinite dilution activity coefficients and predicted those data by the revised ASOG and UNIFAC for solvent (1)/polymer (2) systems. Also, the GC-Flory EOS (group contribution-Flory Equation of State) [Bogdanic and Fredenslund, 1994] was suggested for predicting activity coefficients for polymer solutions by combining the Flory-Huggins model with an equation of state. However, the above mentioned works have some limitations for concentrated copolymer solutions, in spite of having good verification for homopolymer solution systems.

In this work, the activities of solvents were measured by using a gas chromatographic method for solvent/poly(vinylchloride : vinylacetate=88 : 12, wt%) in a temperature range from 398.15 K to 438.15 K. The solvents were benzene, ethylbenzene, chlorobenzene, p-xylene, and n-octane. The group contribution models were modified to predict the activities of solvents for those copolymer solutions. The models have a form which adds the free-volume term and attraction term to the UNIFAC or the ASOG. The results predicted by the various models will also be compared with the experimental data.

EXPERIMENTAL

1. Reagent

For the solvent/poly(vinylchloride : vinylacetate=88 : 12, wt%) system, the copolymer was a polymer copolymerized with VCL (vinylchloride) and VA (vinylacetate). It was obtained from Scientific Polymer Product, Co., and the average molecular

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weight and the dispersity of copolymer were measured by using GPC (CR4A of Shimadzu Co.). The measured values were $M_w=2.2 \times 10^4$, $M_w/M_n=2.83$, respectively. The solvents were special grade reagents from Aldrich Chemical Co. and benzene, ethylbenzene, chlorobenzene, p-xylene, and n-octane. They were used without further purification.

2. Column Preparation

A column was prepared to obtain VLE data for the copolymer solution system by the IGC method. The weighed copolymer [poly(VCL:VA=88:12, wt%)] was dissolved in tetrahydrofuran (THF) at room temperature. The solid support (Fluoropak-80, 40/60 mesh), which could be used regardless of the sample size or the polarity of the solvents, was added to the above copolymer solution. The THF was partially vaporized by heating and stirring on the magnetic stirrer. The mixture was completely dried in the vacuum drying oven through the night, after being set to below the boiling point (75 °C) of THF. The particles were slightly shocked to prevent the coated support from tangling them and to uniformly coat the copolymer on the solid support during the vacuum drying. The dried packing material was packed into the stainless steel column (2 m, ID 3 mm) by using a vibrator. The coating ratio (amount of polymer/amount of support) of the packing material was 8.3 % in this work.

3. Apparatus and Method

A gas chromatographic apparatus was the same one which Kim et al. [1996] used for measuring the infinite dilution activity coefficients of the solvents in homopolymer solutions; but it was different from the point of view of measuring the concentrated activities of copolymer solutions. The apparatus and the experimental procedure, which are described in detail in Kim et al. [1996], consisted of six parts: the carrier gas (He gas), the supplement of solvent, the inverse gas chromatography (IGC), the measurement of pressure between the inlet and outlet in the column, the condenser of solvent, and the measurement of flow rates. The solvent, which was supplied through the rounded flask with the pure carrier gas (He), flowed into the IGC body. The stainless column was wrapped around with a ribbon heater so that the mixed carrier gas was not condensed during the flow process. The IGC was a GC-14B (Shimadzu Co.) equipped with a thermal conductivity detector (TCD). The inlet and outlet pressures of the column in the IGC were measured with a precision pressure gauge (Ashcroft Co. (USA), type 1082). A bubble flow meter was used to measure the flow rate (Q_{He}) of the pure carrier gas after the solvent condensed.

The packed column was incorporated into the IGC and stabilized by the pure carrier gas for 16 hours at the experimental temperature. The flow rates were measured with a bubble flow meter and kept constantly on 0.08 cm³/s in the error range of 0.005 cm³/s. The carrier gas from the bomb passed through the gas diffuser attached on the round flask and swept the solvent vapor and entered into the oil bath. The concentration of the solvents in the mixed carrier gas leaving the oil bath was determined by the saturated pressure of the solvent and the pressure of pure helium. The saturated pressure of the solvent was determined from the Antoine equation [Reid et al., 1987] at the temperature of the oil bath; the

pressure of the pure helium gas was measured by a precision pressure gauge. The concentrations of the solvent in the mixed carrier gas were controlled by raising or lowering the temperature of the oil bath. The solvent-containing air was injected into the port of the IGC by a micro syringe (10 μl) after a constant baseline on the recorder was identified that was regarded as a VLE between the solvent and the copolymer in the IGC column. Therefore, the differences of the retention times between the solvent and the air were read from the recorder (Shimadzu Co. CR6A). Their operations were repeated according to the changes in the temperature of the oil bath in order to measure the next experimental points.

4. Data Reduction

The theoretical relations for computing the desired distribution isotherms from the IGC data were developed in a general form in a series of articles by Conder and Purnell [1968a, b], who demonstrated the utility of their equations by an accurate data reduction of the activity coefficients of n-hexane in squalane and n-heptane in di-n-nonyl phthalate at carrier gas concentrations ranging from zero to 70 mol%. In this work, the technique of elution on a plateau of finite concentration was adopted for performing data reduction. The key equation yields the distribution isotherm: $q(P)$ means mole of solvent per unit mass of polymer in the stationary phase at mean pressure P . To calculate accurate values for the $q(P)$, corrections must be carried out in the experimental values, such as pressure, flow rate, and composition of feed gas. In this work, the derivation of the $q(P)$ was omitted because they have been derived in detail in the literature [Conder and Purnell, 1969a, b; Brockmeier et al., 1972]. The retention volume ($V_s - V_a$) could typically be determined from Eq. (1) by using the retention time ($t_s - t_a$) and the flow rate of the carrier gas.

$$V_s - V_a = \frac{Q_{HE}}{1 - \phi} (t_s - t_a) \frac{273.15}{T_F} \quad (1)$$

The temperature ratio, 273.15/ T_F , was a correction factor to correct the flow rate, Q_{He} , at standard temperature against the room temperature. The retention volume ($V_s - V_a$) was substituted for in Eq. (2) in order to calculate the $q(P)$ in a general form. Therefore, the $q(P)$ was determined with this integral calculation of the retention volume ($V_s - V_a$) and the solvent concentration (c_s) in gas phase on the stationary phase.

$$q(P) = \frac{j}{m_2} \int_0^{c_s} \frac{V_s - V_a}{1 - \phi} dc_s \quad (2)$$

In Figs. 1 and 2 we showed them for the p-xylene/poly(VCL:VA=88:12, wt%) and the ethylbenzene/poly(VCL:VA=88:12, wt%) systems at the experimental temperatures. The $q(P)$ was extended to determine the weight fraction of solvent in copolymer solution and it follows as:

$$w_1 = \frac{q(P)M_1}{1 + q(P)M_1} \quad (3)$$

As a result, the weight fractions (w_1) were used to determine the activities of the solvent based on the weight fraction in the copolymer solutions. We used the equation of Chang and Bonner [1975] to determine it by considering gas-phase non-

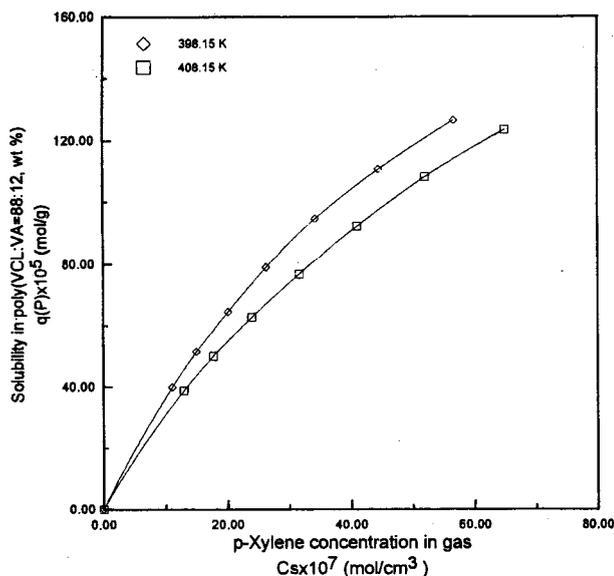


Fig. 1. Distribution isotherms of p-xylene in poly(VCL:VA=88:12, wt%).

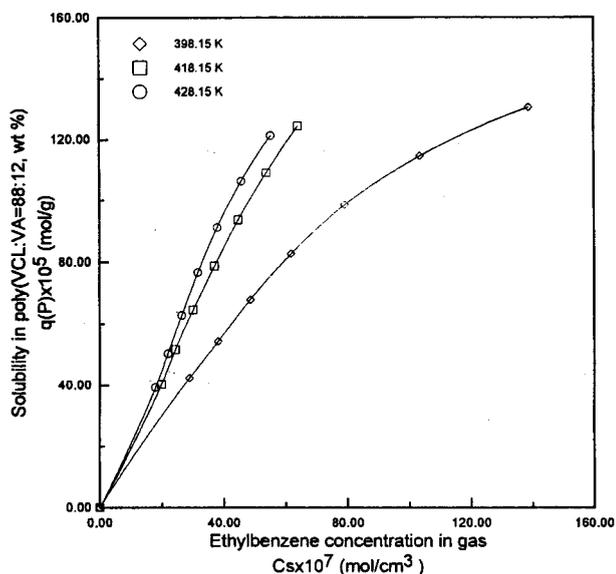


Fig. 2. Distribution isotherms of ethylbenzene in poly(VCL:VA=88:12, wt%).

ideality. Its form was expressed as follows:

$$\Omega_1 = \frac{A_1}{w_1} = \frac{P_o \Psi J_3^4}{w_1 P_1^s} \exp \left[\frac{-B_{11}(P_1^s - P_1)}{RT} \right] \quad (4)$$

The second virial coefficient (B_{11}) was calculated by the Tsonopolous equation [Tsonopolous, 1974, 1975, 1978], and the saturated vapor pressure of the solvent (P_1^s) was estimated by using the Wargner equation or Antoine equation [Reid et al., 1987]. Futhermore, J_3^4 (James-Martin factor), P_1 , and ϕ were calculated by the method of Conder and Purnell [1969a]. Experimental data reduced by Eqs. (1)-(4) are shown in Table 1. Regrettably, experimental data were deficient because unknown problems occurred in the stationary phase [poly(VCL:

Table 1. Experimental activities of each solvent based on the weight fraction for solvent (1)/poly(VCL:VA=88:12, wt%) (2) systems

Solvent	398.15 K		418.15 K		428.15 K	
	w_1	A_1	w_1	A_1	w_1	A_1
Ethylbenzene	0.0297	0.2431	0.0206	0.1793	0.0186	0.1406
	0.0389	0.3024	0.0252	0.2100	0.0227	0.1709
	0.0490	0.3670	0.0309	0.2508	0.0273	0.2030
	0.0616	0.4353	0.0378	0.2973	0.0324	0.2360
	0.0775	0.5054	0.0453	0.3446	0.0387	0.2690
	0.0990	0.5755	0.0540	0.3957	0.0462	0.3260
p-Xylene	0.1284	0.6955	0.0636	0.4476	0.0554	0.3890
	0.0116	0.0927	0.0136	0.1262		
	0.0157	0.1472	0.0185	0.1677		
	0.0209	0.1970	0.0248	0.2148		
	0.0271	0.2368	0.0325	0.2765		
	0.0351	0.2890	0.0417	0.3420		
Benzene	0.0451	0.3436	0.0524	0.4001		
	0.0568	0.4189	0.0645	0.4566		
	0.0253	0.1084	0.0310	0.1120		
	0.0311	0.1384	0.0370	0.1371		
	0.0390	0.1648	0.0439	0.1614		
	0.0497	0.1991	0.0518	0.1846		
n-Octane	0.0579	0.2099	0.0600	0.2166		
	0.0691	0.2593	0.0682	0.2774		
	0.0810	0.2911	0.0711	0.2869		
	0.0154	0.1859	0.0177	0.2006		
	0.0172	0.2023	0.0196	0.2268		
	0.0191	0.2188	0.0214	0.2496		
Chlorobenzene	0.0211	0.2355	0.0234	0.2606		
	0.0234	0.2521	0.0256	0.2738		
	0.0258	0.2686	0.0278	0.3038		
	0.0282	0.2849	0.0299	0.3296		
	0.0120	0.0828				
	0.0159	0.0927				
	0.0206	0.1159				
	0.0262	0.1517				
	0.0326	0.1990				
	0.0400	0.2268				
	0.0484	0.2642				

VA=88:12, wt%)] above 423.15 K. Perhaps the characteristics of poly(VCL:VA=88:12, wt%) disappeared because the experimental temperatures far exceeded the glass temperature (about 356.15 K) of poly(VCL:VA=88:12, wt%).

RESULTS AND DISCUSSION

1. Group Contributions in Copolymer Solutions

Contribution terms that have an influence on thermodynamic properties have been proposed by many researchers when the pure components are dissolved in solutions. Copolymers generally have properties that behave as a single molecule by copolymerizing with functional groups more than two kinds of homopolymers. The poly(VCL:VA=88:12, wt%) was a copolymer that was copolymerized with two homopolymers. In the solid state it behaves as a single molecule, but as two molecules in the solution state. It also has twice the func-

tional group numbers when it is dissolved in the solution. Among group contribution terms, the degrees of the group contribution and the attraction contribution to the thermodynamic properties are similar because the two terms are derived from the functional groups of pure components.

In this work, it was postulated that the two terms have a similar role to compensate each group contribution in the copolymer solutions. The two terms have empirically almost the same values as the copolymers which were divided into two functional groups in their solutions. Therefore, we used empirically four contribution terms which had an effect on the activities of solvents in the copolymer solutions. They are typically classified as the size contribution term, the group contribution term of the original group contribution models (UNIFAC, ASOG), the free volume term, and the attraction term. We have studied the three terms (size, group, free volume) with the exception of the last term (attraction) in previous studies [Choi et al., 1995; Choi et al., 1996; Kim et al., 1996]. In this work, the free volume term and the attractive term were added to the UNIFAC or the ASOG model in order to predict the activities of solvents in solvent (1)/poly(VCL: VA=88:12, wt%) (2) systems. Therefore, a statistical relation to predict the activities of solvents based on the weight fraction in the concentrated copolymer solutions could be represented as Eq. (5) in the case of UNIFAC.

$$A_1 = w_1 \Omega_1 = A_1^C A_1^R A_1^{FV} A_1^{ATT} \quad (5)$$

or

$$\Omega_1 = \Omega_1^C \Omega_1^R \Omega_1^{FV} \Omega_1^{ATT} \quad (6)$$

For the ASOG model, A_1^C and A_1^R (or Ω_1^C , Ω_1^R) were replaced by the A_1^{FH} and A_1^G (or Ω_1^{FH} , Ω_1^G). The size-contribution term caused by the size difference between each molecule was described as $A_1 = w_1 \Omega_1^C$ for the UNIFAC model ($A_1^{FH} = w_1 \Omega_1^{FH}$ for the ASOG model). If Eq. (6) is substituted with Eq. (5), the following equivalent equations are obtained for the UNIFAC model.

$$A_1^C = w_1 \Omega_1^C, \quad A_1^R = \Omega_1^R, \quad A_1^{FV} = \Omega_1^{FV}, \quad A_1^{ATT} = \Omega_1^{ATT} \quad (7)$$

The relation of $A_1^{FH} = w_1 \Omega_1^{FH}$ and $A_1^G = \Omega_1^G$ is obtained for the ASOG model and the others have the same form for the UNIFAC model.

2. Representation of Group Contribution Model

The mole fraction is inadequate for expressing the activities of solvents in polymer solutions because the molecular weight of a polymer is larger than that of a solvent. Therefore, if the UNIFAC (or the ASOG) is transformed into the expression based on the weight fraction, the combinatorial term (the size contribution term in the case of ASOG), and the residual term (the group contribution term in the case of ASOG) can be respectively represented as follows:

2-1. Combinatorial (or Size contribution) Term

2-1-1. UNIFAC Model

$$\ln A_1^C = \ln \Phi_1' + \Phi_2' + \frac{z}{2} M_1 q_1' \ln \frac{\theta_1'}{\Phi_1'} - \frac{z}{2} M_1 q_1' \left(1 - \frac{\Phi_1'}{\theta_1'} \right) \quad (8)$$

$$q_1' = \frac{1}{M_1} \sum_k v_k^{(1)} Q_k \quad (9)$$

$$r_i' = \frac{1}{M_i} \sum_k v_k^{(i)} R_k \quad (10)$$

$$\theta_i' = \frac{q_i' x_i}{\sum_k q_k' x_k} \quad (11)$$

$$\Phi_i' = \frac{r_i' x_i}{\sum_k r_k' x_k} \quad (12)$$

$$x_i = \frac{\frac{w_i}{M_i}}{\sum_k \frac{w_k}{M_k}} \quad (13)$$

where the prime symbol means the amount per unit mass.

2-1-2. ASOG Model

The size contribution term of the ASOG model is represented by Eq. (14) on the basis of weight fraction.

$$\ln A_1^{FH} = \ln \frac{\frac{w_1}{M_1} v_1^{FH}}{\sum_k \frac{w_k}{M_k} v_k^{FH}} + 1 - \frac{\frac{w_1}{M_1} v_1^{FH}}{\sum_k \frac{w_k}{M_k} v_k^{FH}} \quad (14)$$

2-2. Residual (or Group) Term

2-2-1. UNIFAC Model

The residual term of Eq. (7) is represented by Eq. (15) on the basis of the weight fraction in the UNIFAC model.

$$\ln A_1^R = \sum_k v_k^{(1)} [\ln \Gamma_k - \ln \Gamma_k^{(1)}] \quad (15)$$

The activity coefficient (Γ_k) of the k group based on the weight fraction is described in Eqs. (16)-(18) by using $Q_k = M_k Q_k^*$ in the case of the UNIFAC model.

$$\ln \Gamma_k = M_k Q_k^* \left[1 - \ln \left(\sum_m \theta_m' \Psi_{mk} \right) - \sum_m \frac{\theta_m' \Psi_{km}}{\theta_m' \Psi_{mm}} \right] \quad (16)$$

$$\theta_m' = \frac{Q_m' W_m}{\sum_n Q_n' W_n} \quad (17)$$

$$\Psi_{mn} = \exp \left[- \frac{a_{mn}}{T} \right] \quad (18)$$

2-2-2. ASOG Model

If the group contribution term is modified into the expression based on the weight fraction, it can be represented as Eqs. (19)-(22).

$$\ln A_1^G = \sum_k v_{k,1} (\ln \Gamma_k - \ln \Gamma_k^{(1)}) \quad (19)$$

$$\ln \Gamma_k = 1 - \ln \left(\sum_l W_l a_{kl} \right) - \sum_l \frac{W_l a_{lk}}{\sum_m W_m a_{lm}} \quad (20)$$

$$W_k = \frac{\sum_i \frac{w_i}{M_i} v_{ki}}{\sum_i \frac{w_i}{M_i} \sum_l v_{li}} \quad (21)$$

$$\ln a_{kl} = m_{kl} + \frac{n_{kl}}{T} \quad (22)$$

3. Free Volume Term

It is difficult to define accurately the free volume, but it has generally been defined as an inaccessible volume between the volume of the central molecule and other adjacent molecules. The adjacent molecules cannot be held in common when the central molecules are freely changed and rotated in an arbitrary position. To date, a number of free volume theories have been proposed to describe a free volume of polymer solution. For example, there are the works of Iwai et al. [1985], Iwai and Arai [1989], Elbro et al. [1990], and the modified equation of Iwai et al. [1985] using the partition function.

Oishi and Prausnitz [1978] suggested the UNIFAC-FV model for predicting the VLE of polymer solutions. They obtained good results in predicting the VLE for polymer solution systems with a fixation of the external degree of freedom ($C_1=1.1$). Its value was equivalently extended to copolymer solutions of this work but the result was not satisfactory. To obtain better results, we used the predictive type suggested by Bogdanic and Fredenslund [1994], Chen et al. [1990] instead of $C_1=1.1$. It had a form which was represented as a function of temperature as shown in Eq. (24). Therefore, the activity of the solvent was represented as Eqs. (23)-(26) in the UNIFAC or the ASOG model.

$$\ln A_1^{FV} = C_1 \left[3 \ln \left(\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}_m^{1/3} - 1} \right) - \left(\frac{\tilde{v}_1}{\tilde{v}_m} - 1 \right) \left(1 - \frac{1}{\tilde{v}_1^{1/3}} \right)^{-1} \right] \quad (23)$$

$$C_1 = \sum_n v_n \left[C_{T,n} + C_{T,n} \left(\frac{1}{T} - \frac{1}{T_0} \right) + \sum_m \frac{R_n C_n^o}{\sum_m R_m} \right] \quad (24)$$

$$\tilde{v}_i = \frac{v_i}{15.17 b r_i^3}, \quad \tilde{v}_m = \frac{\sum_k v_k w_k}{\sum_i v_i w_i} \quad (25)$$

$$r_i = \frac{1}{M_i} \sum_k (v_k^{(i)} R_k) \quad (26)$$

where T and T_0 are an experimental and an arbitrary reference temperature (298.15 K).

4. Attractive Contribution Term

The attractive term could be described as the attractive potential between two groups. It was represented as a combination of the energy of random orientations and favorable orientations in the Holten-Andersen equation of state [Holten-Andersen et al., 1987], but Chen et al. [1990] and Bogdanic et al. [1994] took into consideration only the random orientation energy to describe it. The models of Chen et al. [1990]

and Bogdanic et al. [1994] are similar to the Flory expression, and the division of a molecule into groups is performed in a similar way as in the UNIFAC model. The functional group parameters of Eq. (24) were estimated from the thermal expansivities, the thermal pressure coefficients (or heat of vaporization) of the pure liquids, and the VLE data for binary mixtures of components with the low molar mass. But those parameters of the UNIFAC were estimated only from the VLE data.

In this work, the attractive term of Bogdanic et al. [1994] was adopted as the contribution term to the activities of solvents in the copolymer solutions and their forms were follows as:

$$\ln A_1^{AT} = \frac{1}{2} z q_i \left\{ \frac{1}{RT} [\epsilon_{ii}(\tilde{v}_m) - \epsilon_{ii}(\tilde{v}_i)] + 1 - \ln \sum_j \theta_j \exp(-\Delta \epsilon_{ji}/RT) - \frac{\sum_i \theta_j \exp(-\Delta \epsilon_{ji}/RT) (\Delta \epsilon_{ji}/RT)}{\sum_k \theta_k \exp(-\Delta \epsilon_{ki}/RT)} \right\} \quad (27)$$

$$q_i = \sum_n v_n Q_n \quad (28)$$

$$\theta_i = \frac{\frac{w_i}{M_i} q_i}{\sum_j \frac{w_j}{M_j} q_j} \quad (29)$$

$$\epsilon_{ji} = \epsilon_{ji}^o / \tilde{v}_m \quad (30)$$

$$\epsilon_{ji}^o = \sum_m \theta_m^{(i)} \sum_n \theta_n^{(j)} \epsilon_{nm} \quad (31)$$

$$\Delta \epsilon_{ji} = \epsilon_{ji} - \epsilon_{ii} \quad (32)$$

Therefore, we summarized four different group contribution models for predicting the VLE of solvent (1)/poly(VCL:VA=88:12, wt%) (2) systems by a combination of Eqs. (8)-(32). They are shown in Table 2.

5. Prediction of Vapor-Liquid Equilibria for Concentrated Copolymer Solutions

The four different group contribution models which could predict the concentrated activities of solvents for solvent (1)/poly(VCL:VA=88:12, wt%) (2) systems are in Table 2. As shown in Table 2, the contribution terms which could have an effect on the activities of solvents in copolymer solutions are divided into combinatorial (or size), residual (or group), free volume, and attractive term. Therefore, we can obtain predictive models such as UNIFAC-FA, ASOG-FA, UNIFAC-FV,

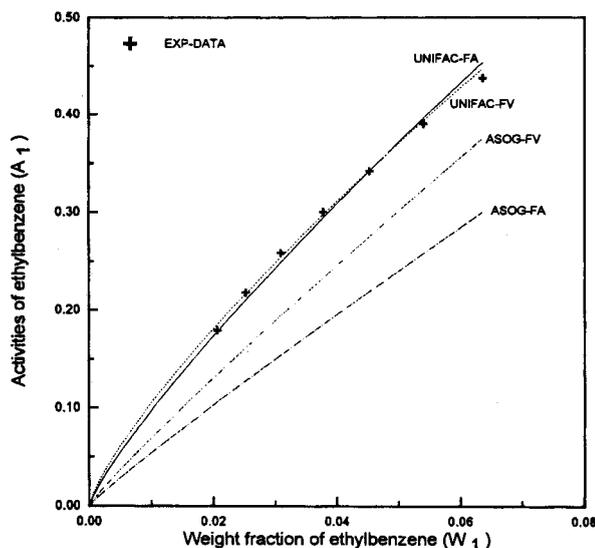
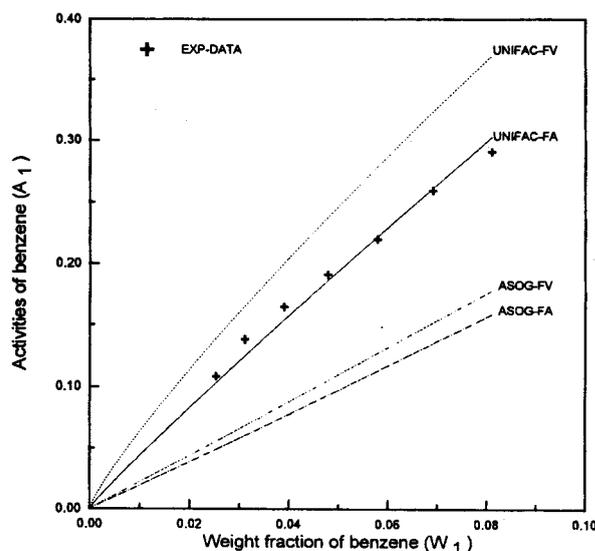
Table 2. Summaries of four different group contribution models for predicting the VLE of solvent (1)/poly(VCL:VA=88:12, wt%) (2) systems

Models	Contribution terms to activity			
	Combinatorial (or Size)	Residual (of Group)	Free volume	Attraction
1. UNIFAC-FA	Eqs. 8-13	Eqs. 15-18	Eqs. 23-26	Eqs. 27-32
2. ASOG-FA	Eq. 14	Eqs. 19-22	Eqs. 23-26	Eqs. 27-32
3. UNIFAC-FV	Eqs. 8-13	Eqs. 15-18	Eqs. 23-26 ($C_1=1.1$)	-
4. ASOG-FV	Eq. 14	Eqs. 19-22	Eqs. 23-26 ($C_1=1.1$)	-

Table 3. Root mean square deviations between the experimental activities and the values predicted by each model for solvent (1)/poly(VCL : VA=88 : 12, wt%) (2) systems

Solvents	398.15 K				418.15 K				428.15 K			
	UNIFAC	ASOG	UNIFAC	ASOG	UNIFAC	ASOG	UNIFAC	ASOG	UNIFAC	ASOG	UNIFAC	ASOG
	-FA	-FA	-FV	-FV	-FA	-FA	-FV	-FV	-FA	-FA	-FV	-FV
Ethylbenzene	1.80	24.46	2.70	4.88	2.58	31.27	1.37	17.25	4.78	27.92	5.09	12.74
p-Xylene	5.81	37.06	5.55	23.59	6.07	37.20	5.90	25.00				
Benzene	4.71	43.02	25.47	37.59	5.57	42.35	27.26	37.73				
n-Octane	8.85	28.85	9.98	15.24	7.04	38.86	10.64	13.37				
Chlorobenzene	5.40	25.98	5.83	5.70								
Total average	5.31	31.87	9.71	17.40	5.32	37.42	11.29	23.34	4.78	27.92	5.09	12.74

$$\text{RMSD}(\%) = \frac{1}{N} \left| \frac{A_1^{\text{exp}} - A_1^{\text{cal}}}{A_1^{\text{exp}}} \right| \times 100$$

**Fig. 3. Comparison of the experimental activities and the predicted values for ethylbenzene (1)/poly(VCL : VA=88 : 12, wt%) (2) system at 418.15 K.****Fig. 4. Comparison of experimental activities and the predicted values for benzene(1)/(VCL : VA=88 : 12, wt%) (2) system at 398.15 K.**

and ASOG-FV by combining those terms to predict the VLE of copolymer solutions. The UNIFAC-FA and the ASOG-FA are based on the UNIFAC and the ASOG, but they are different than the UNIFAC-FV [Oishi and Prausnitz, 1978] and the ASOG-FV [Choi et al., 1995] in two respects.

First, the external degree of freedom (C_1), which plays a major role in determining the free volume contribution, can be predicted by using the known interchange parameters. It is also dependent on temperature. Second, four contribution terms are adopted as contribution terms in copolymer solutions. The UNIFAC-FA or the ASOG-FA have four terms against three contribution terms in the UNIFAC-FV and the ASOG-FV. The values predicted by four different predictive models for solvent/poly(VCL : VA=88 : 12, wt%) systems were compared with the experimental data (see Table 3). As shown in Table 3, the activities predicted by the four models (UNIFAC-FA, ASOG-FA, UNIFAC-FV, and ASOG-FV) agree with experimental data within the error ranges of 1.80-8.85 %, 24.46-43.02 %, 1.37-27.26 %, and 4.88-37.73 %, respectively. To verify the accuracies of the results predicted by the four different

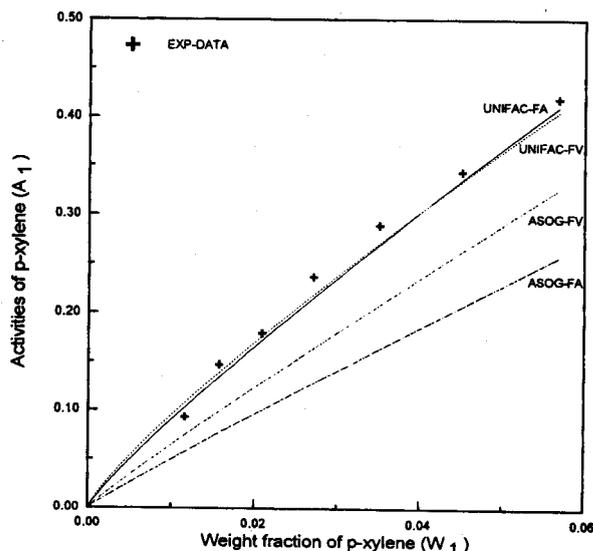
**Fig. 5. Comparison of the experimental activities and the predicted values for p-xylene (1)/poly(VCL : VA=88 : 12, wt%) (2) system at 398.15 K.**

Table 4. Liquid (v_i) and characteristic (v_i^*) molar volumes estimated for the solvents and poly(VCL:VA=88:12, wt%) at experimental temperature

	v_i			v_i^*
	398.15 K	418.15 K	428.15 K	
Ethylbenzene	1.2837	1.3187	1.3374	0.9512
p-Xylene	1.2864	1.3219	-	0.9637
Benzene	1.2929	1.3371	-	0.9000
n-Octane	1.6049	1.6600	1.6902	1.1247
Chlorobenzene	0.9878	1.0130	-	0.7441
Poly(VCL:VA=88:12, wt%)	0.3784	0.3857	0.5851	0.3440

Table 5. External degrees of freedom of solvents predicted for each solvent (1)/poly(VCL:VA=88:12, wt%) (2) system at experimental temperatures

Solvents	External degrees of freedom (C_1)		
	398.15 K	418.15 K	428.15 K
Ethylbenzene	0.3902	0.7833	1.1777
p-Xylene	2.0709	2.5278	
Benzene	1.2704	1.3651	
n-Octane	3.0557	3.5852	
Chlorobenzene	1.6155		

models, the activities vs. weight fraction for the representative ethylbenzene (1)/poly(VCL:VA=88:12, wt%) (2) (418.15 K), benzene (1)/poly(VCL:VA=88:12, wt%) (2) (398.15 K), and p-xylene (1)/poly(VCL:VA=88:12, wt%) (2) (398.15 K) systems were plotted on Figs. 3-5. As shown there, the calculated values agree with the experimental data in the order of UNIFAC-FA, UNIFAC-FV, ASOG-FV and ASOG-FA. The group interaction parameters used in the UNIFAC-FA are the same ones that Gmehling et al. [1982] and Chen et al. [1990] estimated for various groups constituting polymer solutions, and they are the same ones of Tochigi et al. [1990] and Chen et al. [1990] in the case of ASOG-FA. The liquid molar volume (v_i) and the characteristic liquid molar volume (v_i^*) were predicted by the Rackett equation [Reid et al., 1987] for the solvents, and by the group contribution method of Elbro et al. [1991] for the polymer, respectively. The results are shown in Table 4. The external degrees of freedom used in UNIFAC-FA and ASOG-FA were predicted by using the parameters estimated by Bogdanic and Fredenslund [1994], Chen et al. [1990], as shown in Table 5.

CONCLUSIONS

The concentrated activities of solvents based on the weight fraction were measured with the IGC method for copolymer solution systems containing poly(VCL:VA=88:12, wt%) in the ranges of 398.15-438.15 K. The UNIFAC and the ASOG models were slightly revised to predict the activities of solvents in solvent (1)/poly(VCL:VA=88:12, wt%) systems. It was postulated that two terms had a similar role to compensate each group contribution in the copolymer solutions, because the two terms had empirically almost the same values as the copolymers which were divided into two functional groups

in their solutions. Therefore, they consisted of four terms: the combinatorial (or size), the residual (or group), the free volume, and the attractive term. They also interacted with the contribution terms to the activities of solvents in copolymer solutions. The revised models (UNIFAC-FA and ASOG-FA) are different from the UNIFAC-FV and the ASOG-FV in two respects. First, the external degree of freedom of solvent, which plays a major role in determination of the free volume term, is a predictive type. It is predicted from the group interaction parameters instead of the constant value ($C_1=1.1$) in the UNIFAC-FV or the ASOG-FV. Second, an additional attractive term is added to the UNIFAC-FV or the ASOG-FV.

The activities of solvents predicted by the UNIFAC-FA among four models, which could yield excellent results in comparison with other models, agree with experimental data within an error range of 1.80-8.85%. The degree of agreement between the experimental activities and the values predicted by other models was obtained in the order of UNIFAC-FA, UNIFAC-FV, ASOG-FV, ASOG-FA for the solvent (1)/poly(VCL:VA=88:12, wt%) systems.

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NOMENCLATURE

- $A_1, A_1^C, A_1^R, A_1^{FV}, A_1^{ATT}$: activity of combinatorial, residual, free volume, and attractive terms based on weight fraction of component 1
- a_{mn}, a_{kl} : UNIFAC group interaction parameter between group m and n [K]
- b : proportionality factor of order unity [$b=1.28$]
- B_{11} : the 2nd virial coefficient [cm^3/mol]
- c_1, c_s : concentration of solvent [mol/cm^3]
- C_1 : external degree of freedom of solvent [-]
- $C_{T_0^n}$: degree of freedom parameter [-]
- C_{T_n} : degree of freedom parameter [-]
- C_n^0 : degree of freedom parameter [-]
- j : James-Martin pressure correction factor [-]
- m_{kl}, n_{kl} : ASOG parameter between group k, l [-]
- m_2 : weight of polymer [g]
- M_1, M_2, M_i, M_k : molecular weight of component 1, 2, i, k group [g/mol]
- P_1^s, P_b, P_o : saturated vapor pressure, carrier gas pressure of inlet and outlet of column on stationary phase
- Q_{He} : flow rate of pure carrier gas [cm^3/s]
- Q_k, Q_k' : molar group area parameter (k group, k group per unit mass) [-]
- q_1, q_2, q_1', q_2' : van der Waal's surface area (component 1, 2, and van der Waal's surface area of component 1, 2 per unit mass) [-]
- $q(P)$: distribution isotherm of solvent at column pressure P [mol/g]
- R : gas constant [$\text{kPa} \cdot \text{cm}^3/\text{mol} \cdot \text{K}$]
- R_k : molar group volume parameter of k group [-]

r_1, r_2, r_1', r_2' : van der Waals volume (component 1, 2, component 1, 2 per unit mass) [-]
 T, T_F, T_0 : experimental, room, reference temperature [K]
 t_a, t_s : retention time of air and solvent [sec]
 v_i, v_b, \tilde{v}_i : characteristic liquid molar volume, liquid molar volume [cm^3/g], and reduced liquid molar volume of component i [-]
 \tilde{v}_m : reduced volume of polymer solution determined from the equation of state at temperature and pressure of the mixture [-]
 V_s, V_a : retention volume of solvent and air [cm^3]
 w_1 : weight fraction of component 1 [-]
 x_i : mole fraction of component i [-]
 W_m, W_n : weight fraction of group m, n [-]
 z : coordination number [$z=10$]

Greek Letters

$\Delta\epsilon_{ji}$: interaction energy parameter [J/Kmol]
 $\Delta\epsilon_{nm}$: interaction energy between unlike group n and m [J/Kmol]
 ϕ : true value solvent vapor mole fraction on stationary phase [-]
 $\Gamma_k, \Gamma_k^{(1)}$: activity coefficient (group k, group k of pure component 1) based on weight fraction [-]
 $v_k^{(1)}, v_k^{(i)}$: number of group of type k in molecular species 1, i [-]
 θ_m^s, θ_n^s : surface fraction for group m, n [-]
 $\Psi_{km}, \Psi_{mk}, \Psi_{nm}$: UNIFAC parameter between k and m or m and k or n and m [-]
 $\Omega_1, \Omega_1^C, \Omega_1^R, \Omega_1^{FV}, \Omega_1^{ATT}$: activity coefficients (of combinatorial, residual, free volume, attractive terms) based on weight fraction of component 1 [-]

Subscripts

1, s : solvent (volatile, hydrocarbon)
 2 : polymer
 a : air
 i : component i
 k, m, n : group k, m, n

Superscripts

ATT: attraction
 C : combinatorial
 FV : free volume
 R : residual
 S : saturated
 ' : unit mass
 ~ : reduced
 (1), (i) : pure component 1, i

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