

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 2.89×10^5 . Solvents include six aliphatic hydrocarbons such as cyclohexane, methylethylketone, *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 Smidsord 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 ali-

phatic hydrocarbons (cyclohexane, methylethylketone, *n*-hexane, carbontetrachloride, 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, methylethylketone, *n*-hexane, carbontetrachloride, 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 ($\bar{M}_w = 2.89 \times 10^5$, $\bar{M}_w/\bar{M}_n = 1.06$) 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_2) 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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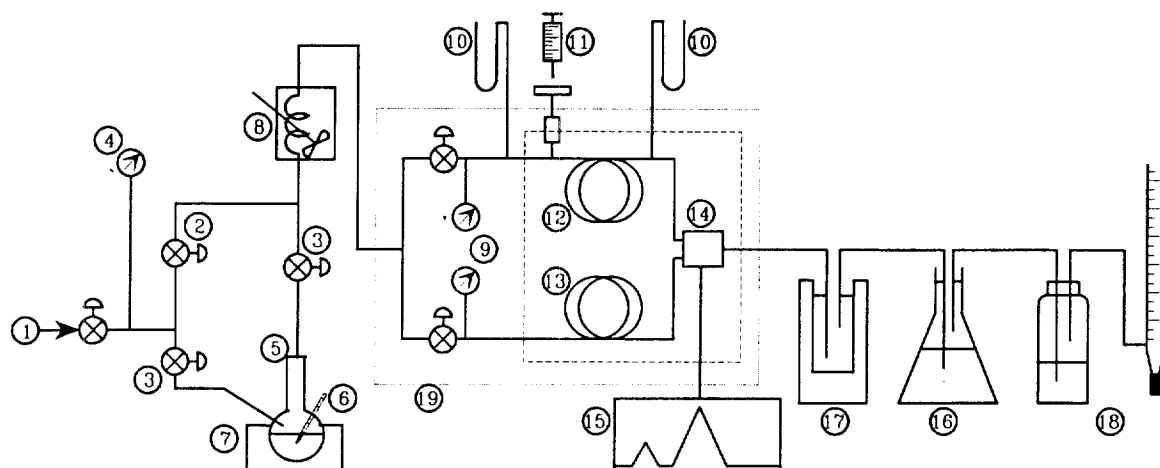


Fig. 1. Schematic diagram of apparatus.

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|-----------------------------|-----------------------|----------------------|------------------------|
| 1. He gas | 6. Thermometer | 11. Micro syringe | 16. Ice condenser |
| 2. Needle valve | 7. Heating mantle | 12. Column | 17. Gas saturator |
| 3. Needle valve | 8. Oil bath | 13. Reference column | 18. Bubble flow meter |
| 4. Precision pressure gauge | 9. Pressure gauge | 14. TCD | 19. Gas chromatography |
| 5. Rounded flask(1 liter) | 10. Mercury manometer | 15. Recorder | |

similar to those of Chang and Bonner [1975], Newman and Prausnitz [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-3BT 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(1)/polymer (2) systems at infinite dilution, the packed column was equipped into IGC and two needle valves (No. ③) 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_{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 μ l) 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].

$$V_g = Q_{He}(t_s - t_a) \frac{273.15 J_3^2}{T_{m_2}} \frac{P_o - P_{H_2O}}{P_o} \quad (1)$$

Therefore the specific retention volumes (V_g) according to changes of the flow rate (Q_{He}) of carrier gas were obtained from Eq. (1) and plotted on Figs. 2 to 4. The specific retention volumes (V_g°) at infinite dilution could also be obtained from Figs. 2 to 4 by extrapolation method. In Eq. (1), J_3^2 known as James-Martin factor

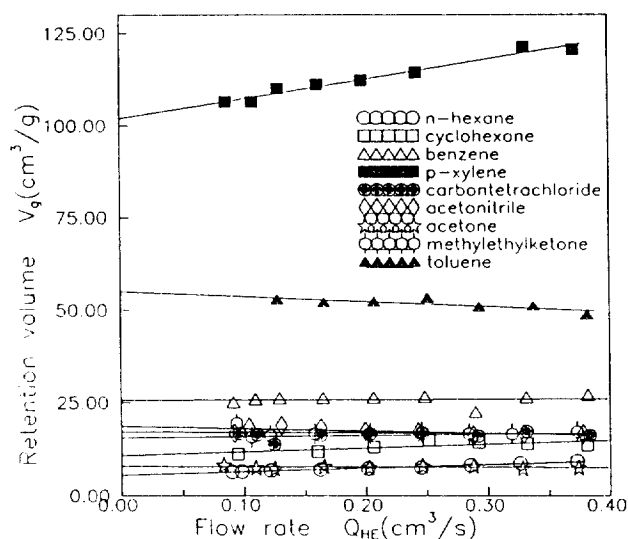


Fig. 2. Relationship between retention volume and flow rate for solvent/polystyrene at 373.15 K.

means a pressure correction factor for the pressure between inlet and outlet of the column and is represented by Eq. (2).

$$J_3^2 = \frac{3}{2} \frac{\left(\frac{P_i}{P_o}\right)^2 - 1}{\left(\frac{P_i}{P_o}\right)^3 - 1} \quad (2)$$

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

$$\Omega_1^\infty = \left(\frac{a_1}{w_1}\right)^\infty = \frac{273.15R}{P_1^\circ V_g^\circ M_1} \exp \left[\frac{-P_1^\circ}{RT} (B_{11} - v_1) \right] \quad (3)$$

Therefore the infinite dilution activity coefficients (Ω_1^∞) of sol-

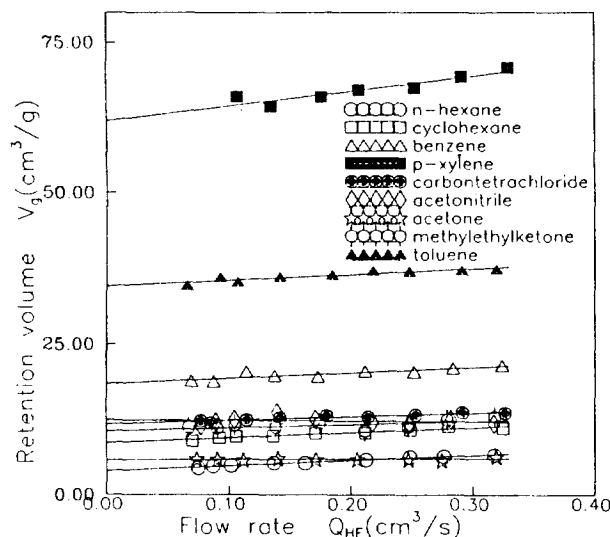


Fig. 3. Relationship between retention volume and flow rate for solvent/polystyrene at 393.15 K.

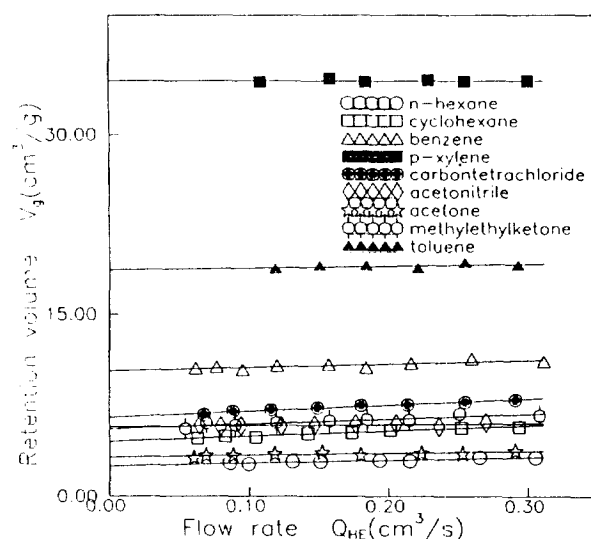


Fig. 4. Relationship between retention volume and flow rate for solvent/polystyrene at 423.15 K.

Table 1. Experimental activity coefficients of solvents based on weight fraction at infinite dilution for solvent(1)/polymer(2) systems

System		Ω_1^∞						
(1)	(2)	373.15	393.15	423.15	448.20	453.00	463.00	473.20(K)
Acetonitrile	Polystyrene	18.74	18.39	19.75/19.8*	19.8**	-	-	19.7**
Acetone	Polystyrene	14.87	13.23	12.89	-	-	-	-
Methylethylketone	Polystyrene	10.59	10.56	10.55/9.44*	-	-	-	-
Cyclohexane	Polystyrene	12.35	12.04	12.26/12.2*	-	-	-	-
n-Hexane	Polystyrene	21.24	19.63	16.99	-	-	-	-
Carbontetrachloride	Polystyrene	5.18	4.65	4.26	-	-	-	-
Benzene	Polystyrene	6.65	5.76	5.46/5.44*	-	4.90**	4.91**	-
Toluene	Polystyrene	6.25	5.64	5.21/5.22*	-	4.99**	4.98**	-
p-Xylene	Polystyrene	6.70	5.71	4.80	-	-	-	-

*Newmann and Prausnitz: *J. of Chem. Phys.*, **76**, 1492 (1972)

**Hao et al.: DECHEMA Chemistry Data Series, Frankfurt (1992)

vents based on the weight fraction at infinite dilution were determined from Eq. (3), and were shown in Table 1 with the reference values [Newman and Prausnitz, 1972; Hao et al., 1992] for testing consistency of experimental data. They were satisfactory within an experimental error of 2.36% by comparing with reference values. The physical properties (P_1^s , B_{11} , v_1) of pure solvents in Eq. (3) were obtained respectively from Antoine [Reid et al., 1987] or Wagner [Reid et al., 1987] equation, Tsonopoulos equation [Tsonopoulos, 1974; 1975; 1978], Rackett equation [Robert et al., 1987].

RESULT AND DISCUSSION

1. Modification of UNIFAC-FV at Infinite Dilution

Oishi and Prausnitz [1978] have proposed the UNIFAC-FV model to predict the activities of solvents for polymer solution systems which a solvent had the range of finite concentration. Their model based on the mole fraction which can predict the activity coefficients of solvents for polymer solution systems has the following form

$$\ln \gamma_1 = \ln \gamma_1^C + \ln \gamma_1^R + \ln \gamma_1^{FV} \quad (4)$$

If the Eq. (4) is combined with the next relationship between

the activity coefficients based on the mole fraction and the weight fraction at infinite dilution,

$$\Omega_1^\infty = \gamma_1^\infty \cdot \frac{M_2}{M_1} \quad (5)$$

the following form of UNIFAC-FV model can be easily derived to calculate the infinite dilution activity coefficient of a solvent based on the weight fraction.

$$\ln \Omega_1^\infty = \left(\ln \gamma_1^{\infty C} + \ln \frac{M_2}{M_1} \right) + \ln \gamma_1^{\infty R} + \ln \gamma_1^{\infty FV} \quad (6)$$

We will choose the original UNIFAC [Fredenslund et al., 1975] and the free volume terms of UNIFAC-FV to represent Eq. (6). If a solvent approaches to the state of infinite dilution and relations of $r_1 = M_1 r_1'$, $r_2 = M_2 r_2' = (PM_2') r_2'$, $q_1 = M_1 q_1'$, $q_2 = M_2 q_2' = (PM_2') q_2'$ for binary polymer solution systems are applied to the original UNIFAC, the combinatorial term $[\gamma_1^{\infty C} + \ln(M_2/M_1)]$ Eq. of (6) is represented as the following equation.

$$\ln \gamma_1^{\infty C} + \ln \frac{M_2}{M_1} \approx 1 + \ln \frac{r_1'}{r_2'} - \frac{Z}{2} M_1 q_1' \left[1 - \frac{r_1' q_2'}{q_1' r_2'} + \ln \left(\frac{r_1' q_2'}{q_1' r_2'} \right) \right] \quad (7)$$

$$r_i' = \frac{1}{M_i} \sum_k (v_k^{(i)} \cdot R_k) \quad (8)$$

Table 2. External degree of freedom obtained with the experimental activity coefficient for solvent(1)/polymer(2) systems

System		C_1						
(1)	(2)	373.15	393.15	423.15	448.20	453.00	463.00	473.20(K)
Acetonitrile	Polystyrene	0.476	0.535	0.773	0.881	-	-	0.982
Acetone	Polystyrene	0.316	0.240	0.322	-	-	-	-
Methylethylketone	Polystyrene	1.610	1.653	1.696	-	-	-	-
Cyclohexane	Polystyrene	1.865	1.897	2.021	-	-	-	-
n-Hexane	Polystyrene	1.531	1.499	1.384	-	-	-	-
Carbontetrachloride	Polystyrene	1.501	1.309	1.358	-	-	-	-
Benzene	Polystyrene	1.377	1.195	1.166	-	1.007	1.023	-
Toluene	Polystyrene	1.495	1.318	1.213	-	1.154	1.158	-
p-Xylene	Polystyrene	1.903	1.581	1.187	-	-	-	-

$$q_i' = \frac{1}{M_i} \sum_k (v_k^{(i)} \cdot Q_k) \quad (9)$$

Where ' means an amount per unit mass.

The residual term ($\gamma_1^{\infty R}$) of Eq. (6) is represented as the following equation.

$$\ln \gamma_1^{\infty R} = \sum_k v_k^{(1)} (\ln \Gamma_k - \ln \Gamma_k^{(1)}) \quad (10)$$

And the activity coefficient Γ_k of k group based on the weight fraction in above Eq. (10) was represented as the following three equations by using $Q_k = M_k Q_k'$.

$$\ln \Gamma_k = M_k Q_k' \left[1 - \ln \left(\sum_m \theta_m' \Psi_{mk} \right) - \sum_n \frac{\theta_m' \Psi_{km}}{\sum_n \theta_n' \Psi_{nm}} \right] \quad (11)$$

$$\theta_m' = \frac{Q_m' W_m}{\sum_n Q_n' W_n} \quad (12)$$

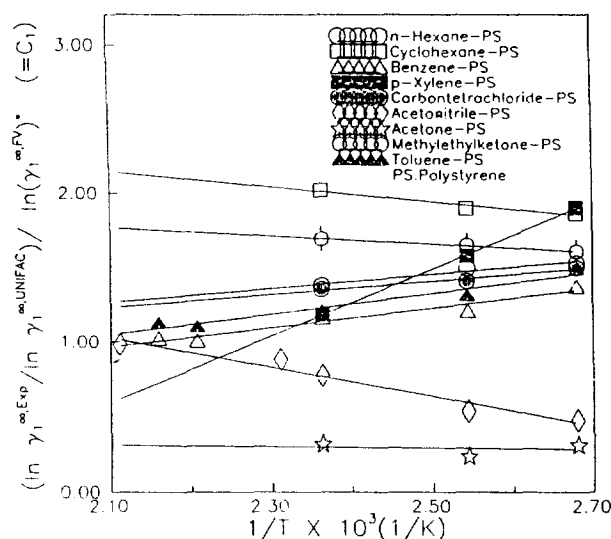
$$\Psi_{mn} = \exp \left(- \frac{a_{mn}}{T} \right) \quad (13)$$

Finally it is difficult to define accurately the free volume term in Eq. (6). Generally speaking, it was defined as a volume that the central molecule and the other adjacent molecules didn't hold in common when the molecules were changed freely or rotated. Until now the various free volume theories have been proposed to represent accurately the free volume of polymer solutions. For example, there were the works of Oishi and Prausnitz [1978], Iwai et al. [1985], Iwai and Arai [1989], Elbro et al. [1990], Kontogeorgis et al. [1993] etc., and the modified equation of Iwai et al. [1985] using the partition function. In this work, we chose the free volume term of Oishi and Prausnitz [1978] in order to predict the activity coefficients of the solvents for solvent(1)/polymer(2) systems at infinite dilution. Their free volume term has the following forms.

$$\ln \gamma_1^{\infty, FV} = C_1 \left[3 \ln \left(\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}_2^{1/3} - 1} \right) - \left(\frac{\tilde{v}_1}{\tilde{v}_2} - 1 \right) \left(1 - \frac{1}{\tilde{v}_1^{1/3}} \right)^{-1} \right] \quad (14)$$

$$\tilde{v}_i = \frac{v_i}{15.17 b r_i'} \quad (15)$$

They have recommended that the VLE for polymer solution systems should be predicted by fixing the external degree of freedom C_1 on 1.1 in free volume term. So we predicted the infinite dilution activity coefficients according to their recommendation using Eq. (6) and represented on Fig. 6. From the Fig. 6, their results were not satisfactory. To improve the results, we inferred the external degree of freedom as a parameter, and it could be determined with the experimental activity coefficients in the range

**Fig. 5. Dependence of temperature on external degree of freedom.**

of experimental temperature from using the ratio of infinite dilution activity coefficients of Eq. (6). The obtained results were shown on Table 2. As shown in Table 2, the external degrees of freedom were increased for the aliphatic hydrocarbons except the *n*-hexane and decreased for the aromatic ones with the raise of temperatures. Bonner and Prausnitz [1973] derived their polymer model from the partition function and described that the external degree of freedom in the free volume was dependent on the temperature. Chen et al. [1990] also demonstrated the temperature dependence on the external degree of freedom. Therefore we propose an empirical free volume term that the external degree of freedom become a function of temperature from their informations. It has a following form.

$$C_1 = A + \frac{B}{T} \quad (16)$$

If $A = 1.1$ and $B = 0$ were applied to Eq. (16), it became a free volume term of Oishi and Prausnitz [1978] at infinite dilution. To examine validity of Eq. (16), we plotted the relationship of the inverse temperature versus the ratio of infinite dilution activity coefficients of Eq. (6) on Fig. 5 and obtained the linearities for all data containing the reference values within an experimental error as shown in Fig. 5. $\ln(\gamma_1^{\infty, FV})^*$ of Fig. 5 was a value of large parenthesis in Eq. (14). Therefore, our assumption was proved to be consistent as shown in Fig. 5.

2. Calculation of Vapor-Liquid Equilibria for Polymer Solu-

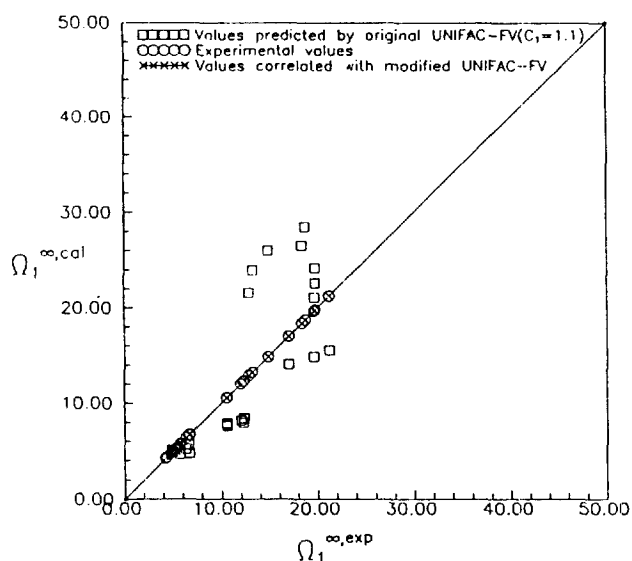


Fig. 6. Comparison with experimental activity coefficients and calculated values.

tions

Oishi and Prausnitz [1978] excellently predicted the VLE with UNIFAC-FV for polymer solution systems which the solvents had the finite concentration. External degree of freedom in the model was $C_1=1.1$. But it is difficult to predict generally the VLE for the polymer solution systems at infinite dilution by that way. Therefore the computational procedures of two steps were performed to improve those problems in this work. The first step was that the activity coefficients of solvent based on the weight fraction were predicted by fixing on $C_1=1.1$. The results were plotted on Fig. 6 with experimental values, but a great deviation was come into existence as shown in Fig. 6. At this time, used model (UNIFAC-FV) was a Eqs. (6) to (15) except Eq. (16). To obtain better results, the modified UNIFAC-FV was combined with a full type of the free volume term ($A \approx B \approx 0$) containing Eq. (16) and it converted into a correlative model. It requires the parameters of original UNIFAC model in order to correlate with the experimental data. Therefore, to determine the new parameters (A, B) of Eq. (16), we used the group interaction parameters of UNIFAC that Gmeling et al. [1982] determined for various functional groups. The parameter estimation was carried out by minimizing the sum of squares between experimental data and those calculated by the modified UNIFAC-FV, and the mathematical algorithm was the Marquardt's method. The new parameters were given with the average deviations in Table 3. The infinite dilution activity coefficients calculated by the modified UNIFAC-FV were agreed with experimental data within an error of 1.24%, and the comparison of results were plotted on Fig. 6. Consequently the modified UNIFAC-FV model may be a convenient and accurate method to correlate VLE data of polymer solutions from the viewpoint of the polymer process modeling, and would become a better predictive model if there were a number of VLE data of polymer solutions. In computational procedures of VLE of polymer solutions, the molar group volume (R_k) and group area (Q_k) parameters were used as the values determined by Gmeling et al. [1982]. The liquid and characteristic liquid molar volumes (v_i, v_i^*) to obtain the reduced liquid molar volumes were predicted by Rackett equation [Robert et al., 1987] for the solvents and

Table 3. Average deviation and parameters estimated by modified UNIFAC-FV for solvent(1)/polymer(2) systems

System		Parameters		RMSD(%)
(1)	(2)	A	B	
Acetonitrile	Polystyrene	3.0634	985.10	2.7984
Acetone	Polystyrene	0.6889	-155.60	2.2887
Methylethylketone	Polystyrene	2.1500	-196.80	0.5166
Cyclohexane	Polystyrene	2.2775	-98.72	0.6720
n-Hexane	Polystyrene	0.1619	517.10	0.9210
Carbontetrachloride	Polystyrene	0.3775	414.44	0.7197
Benzene	Polystyrene	-0.6750	762.28	1.8500
Toluene	Polystyrene	-0.1475	589.80	1.1976
p-Xylene	Polystyrene	-4.1031	0.2283	0.2283
Average				1.2436

$$\text{Average} = \frac{1}{M} \times \text{RMSD} = \frac{1}{M} \left[\sum \left| \frac{\Omega_{1,\infty, \text{CAL}} - \Omega_{1,\infty, \text{EXP}}}{\Omega_{1,\infty, \text{EXP}}} \right| \times 100 \right]$$

Table 4. Liquid and characteristic molar volumes predicted for each solvent and polymer at experimental temperature

Materials	v_i [cm ³ /g]			v_i^* [cm ³ /g]
	373.15K	393.15K	423.15K	
Acetonitrile	1.4385	1.4966	1.6002	0.8846
Acetone	1.4130	1.4745	1.5895	0.8499
Methylethylketone	1.3639	1.4142	1.5045	0.8747
Cyclohexane	1.4096	1.4542	1.5324	0.9336
n-Hexane	1.6977	1.7689	1.9020	1.0140
Carbontetrachloride	0.6957	0.7174	0.7555	0.4279
Benzene	1.2466	1.2848	1.3513	0.7925
Toluene	1.2480	1.2822	1.3405	0.8267
p-Xylene	1.2465	1.2781	1.3314	0.8520
Polystyrene	0.9337	0.9467	0.9663	0.7724

also done by the group contribution method of Elbro et al. [1991] for the polymer, and the predicted liquid and characteristic molar volumes were shown in Table 4.

CONCLUSION

The infinite dilution activity coefficients of solvents based on the weight fraction were measured with the IGC method for polymer solution systems consisting of solvent(1)/polymer(2) systems. They were predicted at infinite dilution by the UNIFAC-FV model proposed by Oishi and Prausnitz [1978] in order to predict the activity coefficient of solvent having a finite concentration in polymer solutions. But the predicted values were not favorably agreed with the experimental data. So we determined the external degrees of freedom according to each system and experimental temperature by using experimental data and the used model was the UNIFAC-FV of Oishi and Prausnitz [1978] at infinite dilution. They were represented as the relation that changed linearly in accordance with the kinds of solvents and the inverse temperature. Therefore the form of C_1 became to $C_1=A+B/T$ and the modified UNIFAC-FV model proposed in this work was converted to the correlative equation having two new parameters at infinite dilution. New parameters A, B were determined by recorrelating the experimental data with the model, and the calculated values agreed with the experimental data within an error of 1.24%.

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NOMENCLATURE

- a_1 : activity of component 1
 a_{mn} : UNIFAC group interaction parameter between group m and n [K]
 A : parameter of modified UNIFAC-FV
 B : parameter of modified UNIFAC-FV
 b : proportionality factor of order unity [$b=1.28$]
 B_{11} : the 2nd virial coefficient [cm^3/mol]
 C_1 : external degree of freedom of solvent
 J_3^2 : James-Martin pressure correction factor
 m_2 : weight of polymer [g]
 M_1, M_2, M_i, M_k : molecular weight of component 1, 2, group i, k [g/mol]
 P : polymerization
 P_1^s, P_i, P_o : saturated vapor pressure, carrier gas pressure of inlet and outlet of column on stationary phase [kPa]
 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 Waals surface area (of component 1, 2 and component 1, 2 per unit mass)
 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 (of component 1, 2 and component 1, 2 per unit mass)
 T : experimental temperature [K]
 t_a, t_s : retention time of air and solvent [sec]
 v_i^*, v_i, \bar{v}_i : characteristic liquid molar volume [cm^3/g], liquid molar volume [cm^3/g], and reduced liquid molar volume of component i
 V_k, V_k^o : specific retention volume, specific retention volume at infinite dilution [cm^3/g]
 w_1 : weight fraction of component 1
 W_m, W_n : weight fraction of group m, n
 Z : coordination number [$Z=10$]

Greek Letters

- $\gamma_1, \gamma_1^C, \gamma_1^R, \gamma_1^{FV}$: activity coefficient (component 1, combinational part, residual part, free volume term) based on mole fraction of component 1
 $\Gamma_k, \Gamma_k^{(1)}$: 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
 Ω_1^∞ : infinite dilution activity coefficient based on weight fraction of component 1
 θ_m', θ_n' : surface fraction for group m, n defined in Eq. (12)
 $\Psi_{km}, \Psi_{mk}, \Psi_{nm}$: UNIFAC parameter between k and m or m and k or n and m defined in Eq. (13)

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