Korean J. Chem. Eng., **20**(4), 745-754 (2003)

Finitely Concentrated Partial Molar Excess Properties of Solvent/Polymer [poly(4-methylstyrene) (PMS), poly(vinylbenzyl chloride) (PVBC)] Systems

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(*Received 1 November 2002 • accepted 28 January 2003*)

Abstract–The finitely concentrated activity coefficients and partial molar excess properties of solvents were measured with inverse gas chromatography (IGC) in polymer solutions containing a poly(4-methylstyrene) (PMS) or a poly(vinylbenzyl chloride) (PVBC). The experimental temperature ranges were 373.15 K to 413.15 K for PMS and 353.15 K to 393.15 K for PVBC. They were over melting point or glass transition temperature of each polymer. Ten kinds of solvents (Acetone, *n*-Heptane, Cyclohexane, Chloroform, Methylisobutylketone, Trichlorobenzene, Benzene, Toluene, Ethylbenzene, Chlorobenzene) that are important in the chemical engineering field were arbitrarily chosen for binary polymer solutions. The external degree of freedom of original UNIFAC-FV model was empirically modified to give flexibility to itself as a $C_1=A+BT$ from the experimental data in finite concentration. The UNIFAC-FV model included a new external degree of freedom as a function of temperature. The parameters (A, B) were estimated by correlating the activities of solvent with the modified model and extended to predict the partial molar excess properties of solvents in the finite-concentrated polymer solutions. The predicted values were compared with them by original UNIFAC-FV as well as the experimental data. The results obtained with the revised model using the new parameter showed the higher quality than the results obtained by original model.

Key words: Inverse Gas Chromatography, Activity Coefficient, Partial Molar Excess Properties, External Degree of Freedom, UNIFAC-FV

INTRODUCTION

The activity coefficients of each solvent play an important role in chemical technology, namely in qualitative and quantitative analysis of processing and application of polymer and are basically applied to evaluate other thermodynamic properties in the polymer solutions. The partial molar excess properties among those properties play an important role to analyze an energy flow in the polymer manufacture process and are essential for thermodynamic analysis of separation processes in chemical engineering. Many researchers have used Inverse gas chromatography (IGC) to measure such properties by [Patterson, 1962; Schuster et al., 1984; Kim et al., 1996, 1998] because it has the merit of reaching the phase equilibria of polymer solutions within a short time. The IGC method that has been used to measure the finitely concentrated thermodynamic properties was suggested by Conder and Purnell [1968a, b, 1969a, b] and continued to be used by Brockmeier et al. [1972], Choi et al. [1995] and Patterson et al. [1983]. The group contribution models to describe the phase behavior of polymer solutions were typically the UNIFAC-FV [Oishi and Prausnitz, 1978], the modified ASOG [Choi et al., 1995], and GC-Flory EOS [Holten-Anderson et al., 1987]. Recently, Kim et al. [1998] modified the UNIFAC-FV to represent the partial molar heat of mixing at infinite dilution in solvent/polymer solutions. In spite of the importance of partial molar excess properties, a systematic predictive method for partial molar excess properties in finite-concentrated polymer solution systems has not yet been established. Many researchers have been measuring them mainly for polymer solution in infinite dilution by IGC method, but due to technical problems, they have not progressed for the method to measure and predict them in finite concentration by IGC method.

In this work, the IGC method was used to measure the finitely concentrated activity coefficients of each solvent in polymer solutions containing PMS or PVBC in the temperature ranges over glass transition temperature of each polymers. The partial molar excess properties will be also evaluated from the activity coefficients. Moreover, original UNIFAC-FV representing the activities of solvent in polymer solutions will be empirically modified from the experimental data for finite-concentrated polymer solutions, and extended to predict the partial molar excess properties, such as partial molar excess enthalpy, partial molar excess Gibbs energy and partial molar excess entropy, of each solvent in polymer solutions. The new parameters will be introduced to measure the fixed external degrees of freedom in UNIFAC-FV model as the temperature-dependent molecular external degrees of freedom. The estimated new parameters from the experimentally measured activity coefficients will be used to predict the partial molar excess properties by UNIFAC-FV.

EXPERIMENTAL

1. Materials

The special grades of poly(4-methylstyrene) and poly(vinylbenzylchloride) were supplied from Aldrich Chemical. The average

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Table 1. Average molecular weight and glass transition temperature of each polymer

Polymers	$\overline{M}_w$	T_g (K)
Poly(4-methylstyrene)	5.5×10^4	366
Poly(vinylbenzyl chloride)	7.2×10^4	295

molecular weight ($\overline{M}_w$) and the glass transition temperatures (T_g) of each polymer were analyzed with GPC (Shimadzu, R4A) and DSC (TA Instruments, DSC 2010), respectively. The temperature repeatability of DSC in this work was ±0.1 °C. The data are presented in Table 1. Solvents (acetone, chloroform, *n*-heptane, cyclohexane, trichloroethylene, benzene, ethylbenzene, chlorobenzene, methylisobutylketone, toluene) were used without further purification as special grades, also supplied from Aldrich Chemical.

2. Measurement of Partial Molar Excess Properties

The preparation of a column is an important factor to accurately measure the partial molar excess properties in polymer solutions. The method was described in detail in the work of Kim et al. [1998] where they carried out the experiment at infinite dilution. Therefore, it will be described briefly in this paper.

The solid support was a Fluoropak 80 (40/60 mesh) and the coating ratios of packing materials were 8.11% and 7.90% for PMS and PVBC, respectively. The apparatus to measure the vapor-liquid equilibria (VLE) in this work and in the work of Kim et al. [1998] was the same except that a solvent supply flask was attached to the apparatus. The solvent was supplied through the gas diffuser attached on the rounded flask as the method fully described in the work of Choi et al. [1995]. Thereafter, the control of solvent concentrations was carried out by ascending or descending temperature of the solvent supply flask. The retention times of air and solvent peak were obtained from the recorder of VLE apparatus of polymer solutions.

The procedures for evaluating the weight fractions were omitted in this work because they were minutely described in the work of Conder and Purnell [1968a, b, 1969a, b] and Brockmeier et al. [1972]. They showed that the distribution isotherm in column was given by the following equation.

$$q(P)=\frac{j}{m_2}\int_0^{C_i}\frac{V_s-V_a}{1-\Psi}dC_S \tag{1}$$

In this work, we used the elution on a plateau method which kept constant concentration in the carrier gas to evaluate q(P). The criterion for constant concentration as given by Conder and Purnell [1969a] is

$$y_0(P_i-P_0)/P_0\le 0.01 \tag{2}$$

where 0.01 is the experimental uncertainty in V_s. If reliable data are to be obtained at high solvent mole fraction, the column pressure drop must be held to a very low value. But, this restriction on pressure drop can be somewhat relaxed for the case of a nearly straight distribution isotherm. With a straight isotherm, the contribution to retention time at the inlet of the IGC column (high C) is exactly offset by the loss at the outlet (low C) of the column. The pressure gradient must be nearly linear. ($P_i/P_0<1.7$) All of q(P) values obtained from the change of C_s were almost linear in those solvent/polymer systems of this work. Experimental error can be generally accepted up to about 5%, in this work, so the limit set by Eq. (2) was extended to 0.01-0.09.

The retention volume (V_s-V_a) in Eq. (1) was typically determined by substituting the retention time (t_s-t_a) and the flow rate of carrier gas (Q_{He}), that are experimentally determined, into the following equation.

$$V_s-V_a=\frac{Q_{He}}{1-\Psi}(t_s-t_a)\frac{T}{T_f} \tag{3}$$

Therefore q(P) is extended into the following equation to determine the weight fraction of solvent (w_1) in polymer solution.

$$w_1=\frac{q(P)M_1}{1+q(P)M_1} \tag{4}$$

The weight fractions were used to determine the finitely concentrated activity coefficients of various solvents. Considering gas phase nonideality, we used the following equation of Chang and Bonner [1975], to determine the activity coefficients.

$$\Omega_1=\frac{A_1}{w_1}=\frac{P_o\Psi J_3^4}{w_1P_1^s}\exp\left[\frac{-B_{11}(P_1^s-P_1)}{RT}\right] \tag{5}$$

In Eq. (5), J_3^4, known as the James-Martin factor, refers to the pressure correction factor for the pressure between inlet and outlet of the column and was represented by Eq. (6):

$$J_n^m=\frac{m}{n}\frac{(P_i/P_o)^n-1}{(P_i/P_o)^m-1} \tag{6}$$

The activities evaluated by Eq. (1)-(5) were compared with those of Choi et al. [1995] for typical benzene(1)/polystyrene(2) systems

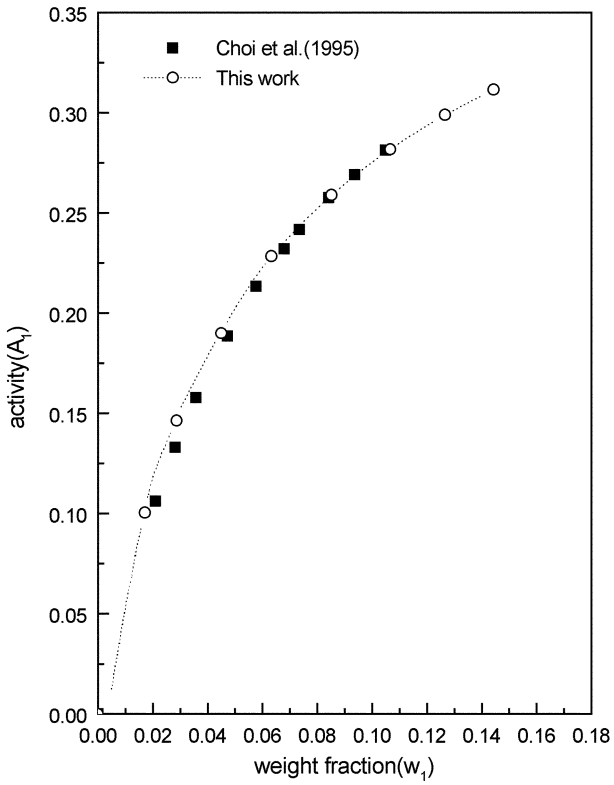

Fig. 1. Comparison of the activities with the cited data for benzene(1)/polystyrene(2) system at 393.15 K.

to verify the accuracy of experimental data. The results were plotted in Fig. 1. As shown in Fig. 1, solvent activities in a variety of concentrated polymer solutions can often be estimated with an uncertainty of no more than ±5% in comparison with typical experimental results. Therefore, other experimental data were assumed to be correct within those experimental error ranges. The activity coefficients were extended to evaluate the partial molar excess properties ($\overline{H}_1^E$, $\overline{G}_1^E$, $\overline{S}_1^E$) of each solvent by the fundamental thermodynamic relations applied at constant pressure and constant weight fraction.

$$\overline{H}_1^E = -RT^2\left(\frac{\partial \ln \Omega_1}{\partial T}\right)_{p,w} = -RT^2\left(\frac{\Delta \ln \Omega_1}{\Delta T}\right)_{p,w} \quad (7)$$

$$\overline{G}_1^E = RT\ln\Omega_1 \quad (8)$$

$$\overline{S}_1^E = \frac{\overline{H}_1^E - \overline{G}_1^E}{T} \quad (9)$$

The second term of Eq. (7) was determined from the third one which represents the slope of a plot between activity coefficient and temperature, because there is linear relationship between $\ln\Omega_1$ and T. The example of plots was representatively shown in Fig. 2 for the benzene(1)/PVBC(2) systems at constant pressure and weight fractions.

The saturated vapor pressures (P_1^s) of pure solvents were estimated by Wagner equation and Antoine equation [Reid et al., 1987] and the second virial coefficient (B_{11}) was calculated from the equation of Tsonopoulos [1974]. Furthermore, J, P_1 and Ψ were calculated by the method of Conder and Purnell [1969a].

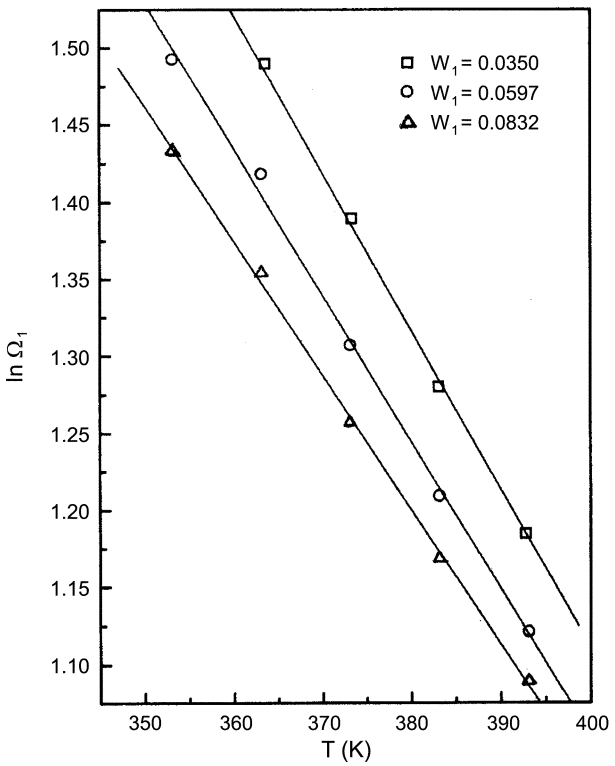

Fig. 2. Temperature dependence on the activity coefficients based on the weight fraction for benzene(1)/poly(vinylbenzyl chloride)(2) system.

RESULTS AND DISCUSSION

1. Partial Molar Excess Properties

Partial molar excess properties were defined as the difference between the actual property of a component in real solution and the value that it would have in an ideal solution at the same temperature, pressure, and composition. The partial molar excess properties obtained from Eqs. (7) to (9) are shown in Table 2. In general, partial molar excess Gibbs energy is an elementary and essential property in fluid phase equilibria. As shown in Table 2, the partial molar excess Gibbs energy decreased with temperature and weight fraction of solvents in all systems. But partial molar excess enthalpy and entropy for PMS increased with temperature and weight fraction of all solvents except for cyclohexane. Cyclohexane, which is a ring compound, for PMS showed that it absorbed heat because the partial molar excess enthalpy decreased with weight fraction of it when it was compared with other solvents. In addition, partial molar excess enthalpy and entropy for PVBC were the same trend as that of PMS except for benzene. Benzene, which was aromatic compound, for PVBC showed the same trend as cyclohexane for PMS.

On the other hand, the experimental partial excess properties of each component in polymer solutions are important factors to determine the total excess properties of polymer solutions. The total excess properties are usually used to describe the behavior of polymer solutions. Most interesting properties among those excess properties are H^E, G^E, and S^E. They are evaluated from partial molar excess properties of each component in polymer solutions. To consider the mutual relation between those experimental data, $\overline{H}_1^E$, $\overline{G}_1^E$, $\overline{S}_1^E$ as a function of the composition changes were representatively plotted in Figs. 3 to 6 for eight polymer solution systems at 373.15 K. From Figs. 3 to 6, $\overline{G}_1^E$ values of PMS solutions were larger than those of PVBC solutions. $\overline{H}_1^E$ and $\overline{S}_1^E$ of PVBC solutions were larger than those of PMS solutions. The tendency of $\overline{G}_1^E$ was also same as the former but $\overline{H}_1^E$ and $\overline{S}_1^E$ were reversely shown in the remaining twelve polymer solution systems. And, solubility parameters [Brandrup and Immergut, 1989] of four solvents (acetone, *n*-heptane, chloroform, chlorobenzene) used in Figs. 3 to 6 exhibited a tendency to above 19.0 $(MPa)^{1/2}$ but those of remaining six solvents were shown as below 19.0 $(cal/cm^3)^{1/2}$. And, solubility parameters of PMS or PVBC were known as above 19.0 $(MPa)^{1/2}$.

In general, the greater the difference in solubility parameters between two liquids, the larger the heat of mixing becomes, and thus the two liquids become less miscible. For this reason the best solvent for a substance is the solute itself.

From the viewpoint of solubility parameters, polymer (PMS or PVBC) solutions of four solvents become more miscible than those of six solvents because the difference in solubility parameters is small. From the viewpoint of partial excess enthalpy, each heat of mixing of polymer (PMS or PVBC) solutions consisting of four solvents becomes larger than that of heat of mixing of polymer (PMS or PVBC) solutions consisting of six solvents. Therefore, we could obtain the result that polymer solutions consisting of four solvents become more miscible than polymer solutions consisting of remaining six solvents from the solubility parameters and heat of mixing data. And exact dissolution between the polymer solutions cannot be described by solubility parameters but miscibilities of polymer

Table 2. Experimental thermodynamic properties of each solvent in solvent(1)/polymer(2) systems

Solvents	w_1	373.15 K				383.15 K				393.15 K				403.15 K				413.15 K			
		Ω_1	$\overline{H}_1^E$	$\overline{G}_1^E$	$\overline{S}_1^E$	Ω_1	$\overline{H}_1^E$	$\overline{G}_1^E$	$\overline{S}_1^E$	Ω_1	$\overline{H}_1^E$	$\overline{G}_1^E$	$\overline{S}_1^E$	Ω_1	$\overline{H}_1^E$	$\overline{G}_1^E$	$\overline{S}_1^E$	Ω_1	$\overline{H}_1^E$	$\overline{G}_1^E$	$\overline{S}_1^E$
Poly(4-methylstyrene)																					
Acetone	0.0453	3.3	8300.3	3685.9	12.4	3.1	8751.2	3639.1	13.3	2.8	9214.0	3379.1	14.8	2.7	9688.6	3264.0	15.9	2.5	10175.2	3138.8	17.0
	0.0541	3.1	9175.0	3457.0	15.3	2.9	9654.4	3358.5	16.4	2.6	10164.9	3072.5	18.0	2.4	10688.6	2930.5	19.2	2.3	11225.4	2777.5	20.5
	0.0633	2.8	10187.3	3217.5	18.7	2.6	10740.6	3076.3	20.0	2.3	11308.6	2782.9	21.7	2.2	11891.2	2604.7	23.0	2.0	12488.4	2374.9	24.5
n-Heptane	0.0115	27.0	16554.4	10219.2	17.0	22.1	17453.6	9864.9	19.8	20.0	18376.5	9800.1	21.8	16.9	19323.2	9471.2	24.4	15.1	20293.7	9325.2	26.6
	0.0210	20.4	17052.2	9355.8	20.6	16.8	17978.4	8978.4	23.5	14.9	18929.1	8829.9	25.7	13.0	19904.3	8517.6	28.2	11.2	20904.0	8305.7	30.5
	0.0310	17.0	17978.3	8791.8	24.6	13.7	18954.8	8340.3	27.7	12.1	19957.1	8155.3	30.0	10.3	20985.3	7825.8	32.6	9.0	22039.3	7554.1	35.1
Cyclo-	0.0176	20.1	26776.4	9313.6	46.8	15.4	28230.8	8701.9	51.0	12.1	29723.7	8143.5	54.9	9.0	31255.0	7377.3	59.2	8.3	32824.7	7250.8	61.9
hexane	0.0245	16.6	26081.8	8707.7	46.6	12.8	27498.5	8111.9	51.0	10.1	28952.6	7570.9	54.4	7.7	30444.2	6823.6	58.6	6.9	31973.3	6649.0	61.3
	0.0339	14.1	25966.1	8210.7	47.6	11.1	27376.4	7665.3	51.5	8.8	28824.1	7112.6	55.2	6.7	30309.1	6837.2	59.3	5.9	31831.3	6098.7	62.3
Chloro-	0.0350	3.2	8439.3	3598.8	13.0	3.0	8897.7	3545.2	14.0	2.8	9368.2	3357.2	15.3	2.5	9850.8	3098.1	16.8	2.4	10345.5	3057.1	17.6
form	0.0597	2.5	10025.2	2880.9	19.2	2.4	10569.8	2725.8	20.5	2.1	11128.7	2488.8	22.0	1.9	11702.0	2178.7	23.6	1.8	12289.8	2056.2	24.8
	0.0832	2.2	11067.1	2397.8	23.2	2.0	11668.3	2175.4	24.8	1.8	12285.3	1909.9	26.4	1.6	12918.2	1585.1	28.1	1.5	13567.0	1374.0	29.5
Methyl-	0.0541	10.6	21057.6	7709.4	35.8	8.5	22201.4	7199.3	39.2	7.2	23375.4	6841.0	42.1	6.0	24579.7	6433.1	45.0	5.0	25814.2	5996.4	48.0
isobutyl	0.0992	8.0	21208.1	6835.1	38.5	6.4	22360.1	6281.2	42.0	5.4	23542.5	5898.6	44.9	4.5	24755.3	5467.1	47.8	3.7	25998.7	5006.4	50.8
ketone	0.1444	6.8	22064.8	6246.9	42.4	5.3	23263.3	5688.1	45.9	4.4	24493.4	5236.7	49.0	3.6	25755.3	4766.6	52.1	3.1	27048.8	4266.5	55.1
Trichloro-	0.1200	2.6	13868.6	2936.4	29.3	2.2	14621.9	2573.2	31.5	2.0	15395.1	2250.1	33.4	1.7	16188.3	1791.2	35.7	1.6	17001.3	1663.5	37.1
benzene	0.1528	2.3	14621.1	2635.8	32.1	2.0	15415..3	2264.6	34.3	1.8	16230.4	1908.2	36.4	1.5	17066.6	1427.5	38.8	1.4	17923.8	1238.3	40.4
	0.1845	2.2	15338.9	2372.7	34.8	1.9	16172.0	1657.8	37.1	1.6	17027.2	1593.5	39.3	1.4	17904.4	1105.1	41.7	1.3	18803.6	841.2	43.5
Benzene	0.0382	5.6	12630.0	5323.7	19.6	4.8	13316.0	4963.7	21.8	4.1	14020.1	4577.1	24.0	3.9	14742.4	4522.2	25.4	3.6	15482.8	4379.2	26.9
	0.0493	5.0	13220.4	4992.3	22.1	4.3	13938.4	4608.5	24.4	3.6	14675.5	4152.2	26.8	3.4	15431.6	4133.1	28.0	3.1	16206.6	3932.7	29.7
	0.0600	4.6	13486.6	4700.0	23.6	3.9	14219.2	4293.1	25.9	3.2	14971.1	3828.6	28.3	3.1	15742.3	3785.9	29.7	2.8	16533.0	3576.8	31.4
Toluene	0.1003	4.8	15882.9	4893.1	29.5	4.2	16745.6	4561.7	31.8	3.6	17631.2	4222.8	34.1	3.2	18593.5	3893.8	36.3	2.8	19470.6	3526.0	38.6
	0.1548	4.1	16867.0	4385.8	33.5	3.5	17783.1	3993.0	36.0	3.0	18723.5	3622.6	38.4	2.6	19688.1	3244.9	40.8	2.3	20676.9	2843.8	43.2
	0.2108	3.6	17515.2	3987.2	36.3	3.1	18466.6	3583.7	38.8	2.6	19433.1	3169.9	41.4	2.3	20444.8	2763.9	43.9	2.0	21471.6	2333.7	46.3
Ethyl-	0.1106	8.0	20825.1	6466.9	38.5	6.3	21957.3	5861.7	42.0	5.3	23118.4	5420.1	45.0	4.4	24309.4	4982.8	47.9	3.9	25530.4	4677.7	50.5
benzene	0.1849	6.5	21659.6	5813.5	42.5	5.2	22836.1	5224.2	46.0	4.2	24043.7	4714.7	49.2	3.6	25282.4	4242.4	52.2	3.1	26552.1	3865.3	54.9
	0.2501	5.8	22446.8	5475.0	45.5	4.6	23666.0	4826.7	49.2	3.8	24917.5	4323.8	52.4	3.1	26201.2	3806.6	55.6	2.7	27517.1	3383.1	58.4
Chloro-	0.1941	3.8	12919.4	4115.9	23.6	3.3	13621.1	3773.6	25.7	2.9	14341.4	3509.6	27.6	2.6	15080.2	3227.1	29.4	2.4	15837.6	3021.4	31.0
benzene	0.2505	3.5	13845.5	3872.1	26.7	3.0	14597.5	3512.3	28.9	2.7	15369.4	3184.6	31.0	2.4	16161.2	2893.9	32.9	2.2	16972.9	2644.2	34.7
	0.3019	3.3	14528.5	3700.2	29.0	2.8	15317.6	3302.4	31.6	2.5	16217.6	2969.6	33.5	2.2	16958.5	2638.5	35.5	2.0	17810.2	2370.4	37.4

Table 2. Continued

Solvents	w_1	373.15 K				383.15 K				393.15 K				403.15 K				413.15 K			
		Ω_1	$\overline{H}_1^E$	$\overline{G}_1^E$	$\overline{S}_1^E$	Ω_1	$\overline{H}_1^E$	$\overline{G}_1^E$	$\overline{S}_1^E$	Ω_1	$\overline{H}_1^E$	$\overline{G}_1^E$	$\overline{S}_1^E$	Ω_1	$\overline{H}_1^E$	$\overline{G}_1^E$	$\overline{S}_1^E$	Ω_1	$\overline{H}_1^E$	$\overline{G}_1^E$	$\overline{S}_1^E$
Poly(vinylbenzyl chloride)																					
Acetone	0.0660	2.1	12639.6	2229.4	29.5	1.8	13365.5	1729.7	32.0	1.6	14111.7	1438.3	34.0	1.5	14878.2	1272.0	35.5	1.3	15665.0	772.7	37.9
	0.0854	2.0	13375.8	2000.7	32.2	1.6	14144.0	1423.3	35.0	1.4	14933.7	1090.2	37.1	1.3	15744.8	941.96	38.6	1.1	16577.4	406.3	41.1
	0.1048	1.8	13593.5	1782.5	33.4	1.5	14374.2	1134.3	36.5	1.3	15176.8	833.30	38.4	1.2	16001.1	650.8	40.1	1.0	16847.3	121.3	42.5
n-Heptane	0.0198	28.9	15335.5	9875.2	15.5	24.5	16216.3	9653.4	18.1	21.2	17121.6	9470.6	20.5	18.9	18051.6	9366.0	22.7	15.7	19006.2	8997.6	25.5
	0.0291	24.1	16102.7	9348.2	19.1	20.5	17027.6	9111.7	21.8	17.3	17978.3	8847.3	24.5	15.3	18954.8	8692.0	26.8	12.8	19957.1	8340.9	29.6
	0.0381	21.1	16444.9	8947.1	21.2	17.8	17389.4	8699.3	23.9	15.0	18360.3	8390.4	26.7	13.2	19357.6	8222.8	29.1	11.1	20381.2	7859.5	31.9
Cyclo-	0.0228	19.0	18694.9	8637.4	28.5	15.5	19768.7	8276.9	31.6	12.8	20872.4	7902.0	34.8	10.7	22006.1	7553.2	37.7	9.3	23169.8	7274.1	40.4
hexane	0.0350	15.3	19140.8	8004.7	31.5	12.4	20240.2	7607.9	34.8	10.2	21370.2	7214.6	37.9	8.5	22530.9	6827.8	41.0	7.3	23722.4	6509.8	43.8
	0.0470	13.2	19576.3	7570.7	34.0	10.6	20700.7	7125.1	37.4	8.7	21856.4	6699.9	40.6	7.2	23043.6	6299.0	43.7	6.2	24262.1	5967.6	46.5
Chloro-	0.1054	1.8	10306.6	1747.3	24.2	1.6	10898.5	1488.2	25.9	1.5	11507.0	1249.0	27.5	1.4	12132.1	956.9	29.2	1.2	12773.6	635.4	30.9
form	0.1450	1.6	11322.7	1382.0	28.2	1.4	11973.1	1077.0	30.0	1.3	12641.5	777.8	31.8	1.2	13328.2	460.6	33.6	1.0	14033.0	100.4	35.4
	0.1842	1.5	11737.5	1080.2	30.2	1..3	12411.6	719.2	32.2	1.2	13104.6	434.3	34.0	1.0	13816.4	83.1	35.9	0.9	14547.0	−300.1	37.8
Methyl-	0.2352	3.9	14661.5	4018.0	30.1	3.4	15503.6	3689.5	32.5	2.9	16369.2	3336.9	34.9	2.6	17258.3	3005.5	37.2	2.2	18170.9	2612.9	39.3
isobutyl	0.3202	3.6	15812.4	3780.2	34.1	3.1	16720.6	3402.1	36.7	2.6	17654.2	2997.2	39.3	2.3	18613.1	2622.3	41.7	2.0	19597.3	2212.2	44.2
ketone	0.4153	3.4	17077.4	3612.6	38.1	2.9	18058.3	3186.5	41.0	2.4	19066.5	2753.4	43.7	2.1	20102.1	2326.7	46.4	1.8	21165.1	1861.8	49.1
Trichloro-	0.1259	2.9	11706.4	3157.8	24.2	2.6	12378.7	2875.2	26.2	2.3	13069.9	2635.8	28.0	2.1	13779.8	2340.1	29.9	1.9	14508.4	2025.3	31.8
benzene	0.2008	2.5	13075.1	2665.4	29.5	2.2	13826.0	2331.5	31.7	1.9	14598.0	2013.4	33.7	1.7	15390.9	1661.9	35.9	1.5	16204.7	1316.0	37.9
	0.2826	2.2	14516.3	2291.3	34.6	1.9	15350.1	1934.7	36.9	1.6	16207.1	1542.2	39.3	1.4	17087.4	1138.5	41.6	1.3	17991.0	725.3	43.9
Benzene	0.0495	4.8	10109.6	4600.6	15.6	4.4	10690.2	4464.5	17.1	4.0	11287.1	4285.0	18.8	3.6	11900.2	4059.6	20.5	3.3	12529.4	3862.2	22.1
	0.0596	4.5	9871.1	4382.4	15.5	4.1	10438.0	4282.2	17.0	3.7	11020.8	4054.5	18.7	3.4	11619.4	3852.6	20.3	3.1	12529.4	3664.8	22.6
	0.0699	4.2	9052.0	4207.4	13.7	3.9	9571.9	4088.3	15.1	3.5	10106.3	3898.4	16.6	3.2	10655.2	3722.0	18.1	3.0	11218.7	3561.2	19.5
Toluene	0.1933	4.5	13728.3	4391.5	26.4	4.0	14513.8	4183.8	28.5	3.4	15327.3	3823.7	30.8	3.0	16159.8	3525.7	33.0	2.7	17014.3	3181.1	35.2
	0.2459	4.1	14578.5	4159.0	29.5	3.6	15415.9	3885.1	31.8	3.1	16276.6	3504.8	34.2	2.7	17160.6	3198.3	36.4	2.4	18068.1	2793.7	38.9
	0.3021	3.9	15677.6	3962.8	33.2	3.4	16578.1	3659.9	35.6	2.9	17503.7	3260.9	38.2	2.5	18454.4	2897.9	40.6	2.1	19430.3	2434.2	43.2
Ethyl-	0.2806	6.1	16092.4	5295.5	30.6	5.3	17016.6	5018.3	33.04	4.4	17966.7	4597.9	35.8	3.8	18942.6	4281.0	38.3	3.3	19944.3	3879.2	40.9
benzene	0.3458	5.8	16745.6	5155.2	32.8	5.0	17707.4	4850.4	35.4	4.1	18696.0	4398.9	38.3	3.6	19711.5	4078.7	40.8	3.0	20753.9	3633.1	43.6
	0.4098	5.6	17637.3	5062.7	35.6	4.8	18650.3	4707.9	38.4	4.0	19691.6	4264.8	41.3	3.4	20761.2	3878.7	44.1	2.8	21859.0	3414.8	46.9
Chloro-	0.2731	4.0	14049.7	4092.3	28.2	3.5	14856.7	3757.4	30.6	3.0	15686.1	3409.8	32.9	2.7	16538.2	3125.9	35.0	2.3	17412.7	2770.8	37.2
benzene	0.3459	3.8	13935.7	3903.8	28.4	3.2	14736.1	3504.4	30.9	2.9	15558.8	3247.3	33.0	2.5	16403.9	2921.4	35.2	2.2	17271.3	2548.2	37.5
	0.4166	3.6	14257.1	3794.3	29.6	3.1	15076.0	3391.5	32.2	2.7	15917.7	3131.5	34.3	2.4	16782.3	2777.5	36.6	2.1	17669.7	2387.8	38.9

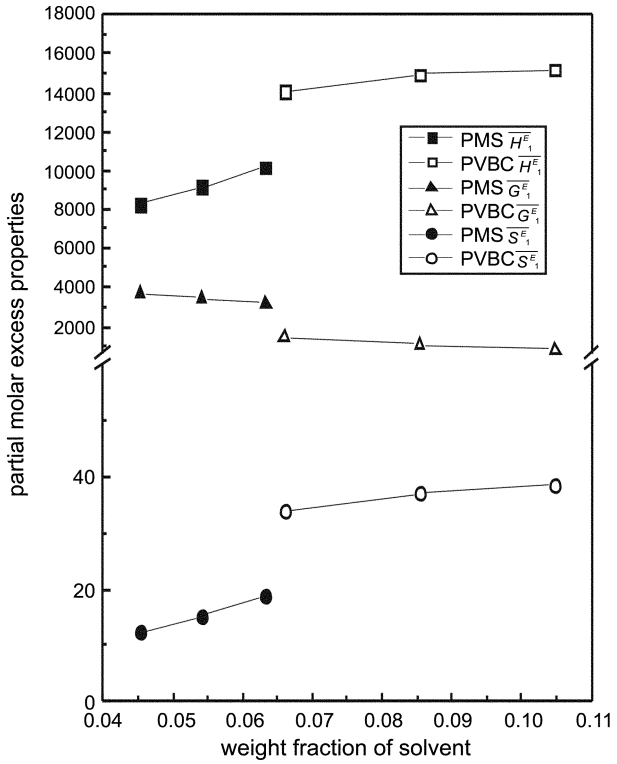

Fig. 3. Partial molar excess properties as a function of weight fraction of solvent for acetone/polymer systems at 373.15 K.

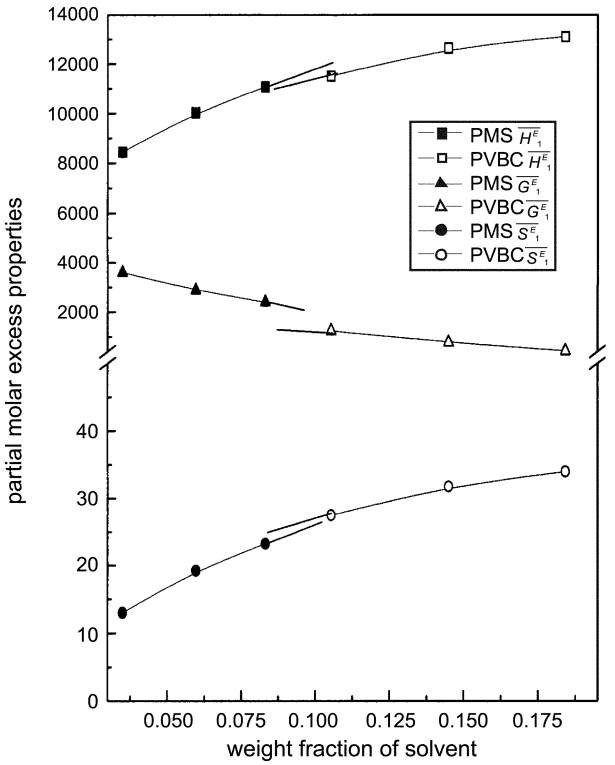

Fig. 5. Partial molar excess properties as a function of weight fraction of solvent for chloroform/polymer systems at 373.15 K.

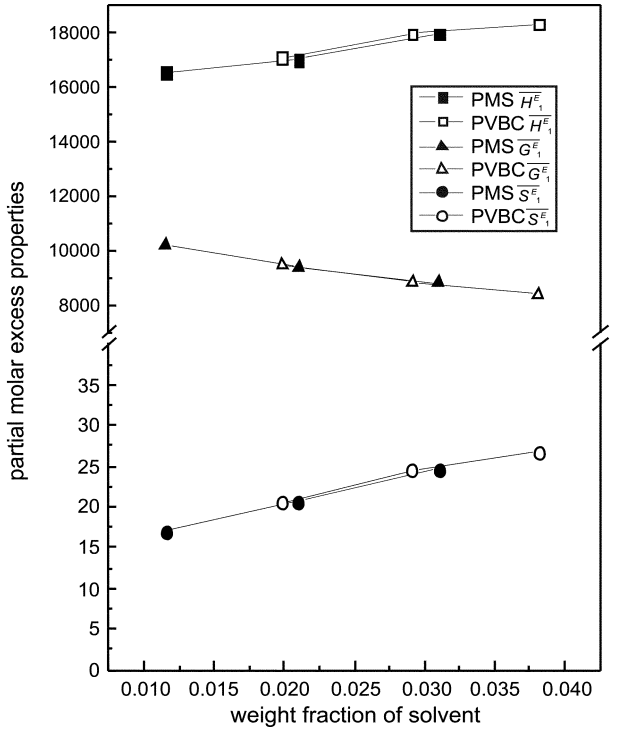

Fig. 4. Partial molar excess properties as a function of weight fraction of solvent for *n*-heptane/polymer systems at 373.15 K.

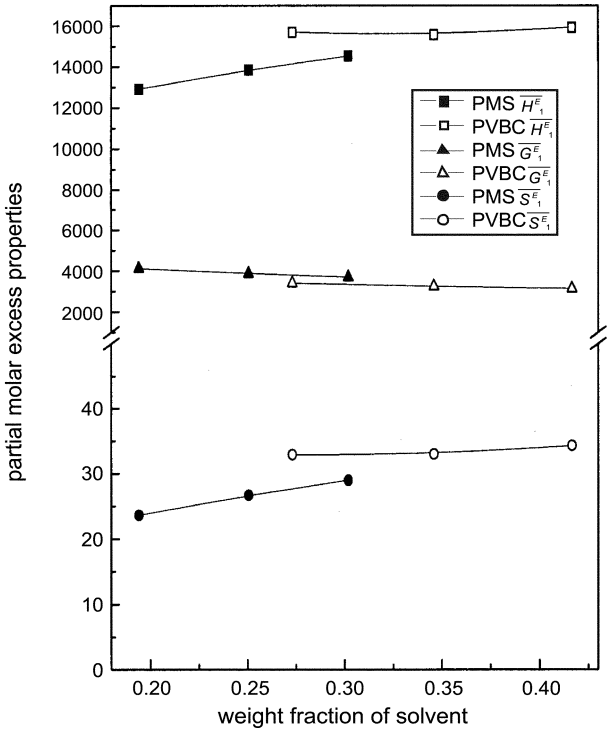

Fig. 6. Partial molar excess properties as a function of weight fraction of solvent for chlorobenzene/polymer systems at 373.15 K.

solutions could be confirmed by them. It showed that four solvents had better dissolution feasibility than those of remaining six solvents for PMS or PVBC.

2. Representation of Activities

The UNIFAC-FV model of Oishi and Prausnitz [1978] has been

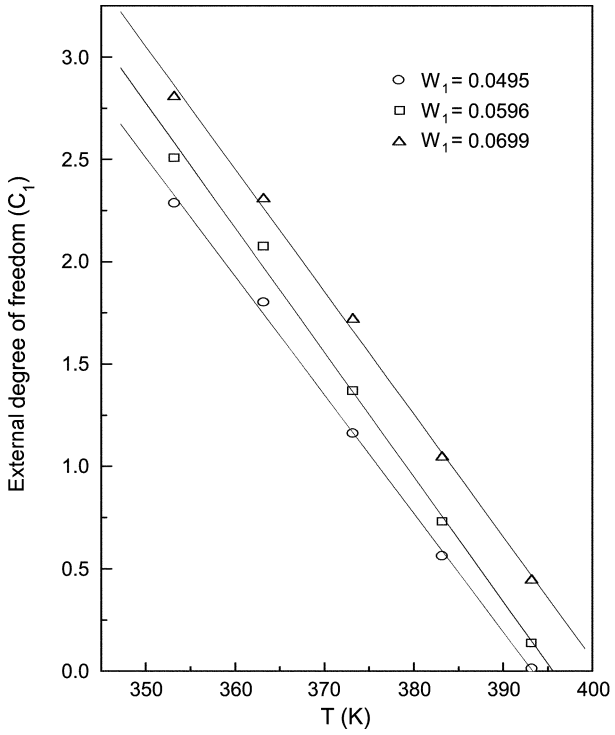

Fig. 7. Temperature dependence on the external degree of freedom for benzene(1)/poly(vinylbenzyl chloride)(2) system.

typically used to predict the activities of solvent in polymer solutions. Its representation of activity based on weight fraction was expressed as Eqs. (10) to (18) as follows:

$$\ln A_1 = \ln A_1^C + \ln A_1^R + \ln A_1^{FV} \tag{10}$$

$$\ln A_1^C = \ln\phi_1' + \phi_2' + \frac{z}{2} M_1 q_1' \ln\frac{\theta_1'}{\phi_1'} - \frac{z}{2} M_1 q_1' \left(1 - \frac{\theta_1'}{\phi_1'}\right) \tag{11}$$

$$\phi_i' = \frac{r_i' w_i}{\sum_j r_j' w_j},\ \theta_i' = \frac{q_i' w_i}{\sum_j q_j' w_j} \tag{12}$$

$$r_i' = \frac{1}{M_i}\sum_k \nu_k^{(i)} R_k,\ q_i' = \frac{1}{M_i}\sum_k \nu_k^{(i)} Q_k \tag{13}$$

$$\ln A_1^R = \sum_k \nu_k^{(1)} [\ln\Gamma_k - \ln\Gamma_k^{(1)}] \tag{14}$$

$$\ln\Gamma_k = M_k Q_k' \left[1 - \ln\left(\sum_m \Theta_m' \Psi_{mk}\right) - \sum_m \left(\frac{\Theta_m' \Psi_{km}}{\sum_n \Theta_n' \Psi_{nm}}\right)\right] \tag{15}$$

$$\Theta_m' = \frac{Q_m' W_m}{\sum_n Q_n' W_n},\ \Psi_{mn} = \exp\left[-\frac{a_{mn}}{T}\right],\ Q_k' = \frac{Q_k}{M_k} \tag{16}$$

$$\ln A_1^{FV} = 3C_1 \ln\left[\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}_M^{1/3} - 1}\right] - C_1\left[\left(\frac{\tilde{v}_1}{\tilde{v}_M} - 1\right)\left(1 - \frac{1}{\tilde{v}_1^{1/3}}\right)^{-1}\right] \tag{17}$$

$$\tilde{v}_1 = \frac{v_1}{15.17 b r_1'},\ \tilde{v}_M = \frac{v_1 w_1 + v_2 w_2}{15.17 b (r_1' w_1 + r_2' w_2)} \tag{18}$$

The UNIFAC-FV model showed good results for the average errors between the experimental and the predicted values in the work of Oishi and Prausnitz [1978] but had a limitation to be not available for all polymer solutions. First, we predicted the finitely concentrated activity coefficients according to a recommendation (C_1= 1.1) of Oishi and Prausnitz by using Eqs. (10) to (18) but could not obtain satisfactory results because C_1 was set equal to 1.1 in the model as suggested by earlier results [Beret et al., 1975] in spite of the presence of different values of C_1 for other solvents containing large molecules. In dependence on the external degree of freedom, High and Danner [1990] also have shown that the C_1 parameter relating the number of external degrees of freedom resulting from the rotation and vibration of the molecules was found to be a linear function of temperature. Chen et al. [1990] also have suggested a new correlation for the C_1 parameter and introduced the simple and linear temperature dependency of the C_1 parameter of the Holten-Andersen et al. [1987] model. Therefore, the preceding results offer a great deal of important information about determination of the external degree of freedom from the experimental data in our work. To give the flexibility to the original UNIFAC-FV model, the external degrees of freedom were determined from the experimental data. That is to say, we plotted representatively the external degree of freedoms according to a variation of temperature on Fig. 3 for benzene(1)/PVBC(2) system. As shown in Fig. 3, the relation between the external degree of freedom and the temperature showed a linear form at each constant concentration. From those results, the external degree of freedom could be obtained as following form.

$$C_1 = A + BT \tag{19}$$

The parameters (A, B) of Eq. (19) were estimated by correlating the finitely concentrated activities of each solvent in the polymer solutions with Eq. (10) and extended to predict the partial molar excess properties. The mathematical algorithm to estimate the parameters was the Marquardts method and the estimated results shown on Table 3. In the computational procedures, the molar group volume (R_k), the group area (Q_k), and UNIFAC group interaction parameter (a_{mn}) were cited from the results of Gmehling et al. [1982]. The liquid molar volumes (v_i) were obtained from Rackett equation from the work of Reid et al. [1987] for each solvent and also done from the method of Elbro et al. [1991] for the PMS and the PVBC.

3. Prediction of Partial Molar Excess Properties

The models containing two parameters (A, B) to describe the temperature-dependent molecular external degree of freedom parameter (C_1) to predict the partial molar excess properties at constant pressure and weight fraction could be evaluated by substituting Eq. (10) to Eqs. (7) to (9). Therefore, the model that could predict the partial molar excess enthalpy ($\overline{H}_1^E$) was expressed by substituting Eq. (10) for Eq. (7) as following.

$$\overline{H}_1^E = -RT^2\left[\left(\frac{\partial \ln\Omega_1^R}{\partial T}\right)_{P,w} + \left(\frac{\partial \ln\Omega_1^{FV}}{\partial T}\right)_{P,w}\right] \tag{20}$$

The partial molar excess Gibbs energy ($\overline{G}_1^E$) and entropy ($\overline{S}_1^E$) could be also expressed by substituting Eq. (10) to Eq. (8) and (9), respectively. The estimated parameters (A, B) were extended to predict the partial molar excess properties ($\overline{H}_1^E$, $\overline{G}_1^E$, $\overline{S}_1^E$) of each solvent in polymer solutions containing PMS or PVBC. Each range of deviation between the values evaluated by experiment and values predicted by original UNIFAC-FV, and of the former and predicted values of the partial molar excess properties by the correlation in this work are listed on Table 4. As shown in Table 4, there

Table 3. Parameters estimated by modified UNIFAC-FV model for solvent(1)/polymer(2) systems

Solvents	w_1	A	B	w_1	A	B
		poly(4-methylstyrene)*			**poly(vinylbenzyl chloride)****	
Acetone	0.0453	4.90	−0.01	0.0660	26.54	−0.07
	0.0541	5.75	−0.01	0.0854	30.39	−0.08
	0.0633	6.74	−0.02	0.1048	33.60	−0.09
n-Heptane	0.0115	7.82	−0.02	0.0198	28.56	−0.06
	0.0210	8.38	−0.02	0.0291	30.57	−0.07
	0.0310	9.27	−0.02	0.0381	31.21	−0.07
Cyclohexane	0.0176	17.18	−0.04	0.0228	62.68	−0.15
	0.0245	17.06	−0.04	0.0350	64.54	−0.16
	0.0339	17.42	−0.04	0.0470	71.07	−0.18
Chloroform	0.0350	5.20	−0.01	0.1054	30.09	−0.07
	0.0597	6.33	−0.01	0.1450	34.77	−0.08
	0.0832	7.50	−0.02	0.1842	38.82	−0.10
Methylisobutyl ketone	0.0541	6.04	−0.01	0.2352	84.45	−0.21
	0.0992	7.39	−0.02	0.3202	127.05	−0.32
	0.1444	9.30	−0.02	0.4153	204.99	−0.52
Trichloroethylene	0.1200	10.44	−0.03	0.1259	42.69	−0.11
	0.1528	12.06	−0.03	0.2008	55.70	−0.14
	0.1845	13.98	−0.03	0.2826	75.10	−0.19
Benzene	0.0382	16.08	−0.04	0.0495	23.97	−0.06
	0.0493	16.42	−0.04	0.0596	24.08	−0.06
	0.0600	16.53	−0.04	0.0699	22.77	−0.06
Toluene	0.1003	13.08	−0.03	0.1933	73.75	−0.19
	0.1548	17.50	−0.04	0.2459	93.93	−0.24
	0.2108	22.85	−0.06	0.3021	124.65	−0.32
Ethylbenzene	0.1106	660.87	−1.60	0.2806	145.53	−0.35
	0.1849	782.88	−1.89	0.3458	193.89	−0.46
	0.2501	966.85	−2.34	0.4098	264.96	−0.63
Chlorobenzene	0.1941	15.53	−0.04	0.2731	96.35	−0.24
	0.2505	18.08	−0.04	0.3459	120.10	−0.30
	0.3019	24.78	−0.06	0.4166	158.35	−0.40

*poly(4-methylstyrene) experiment temperature (K) is 373.15-413.15.
**poly(vinylbenzyl chloride) experiment temperature (K) is 353.15-393.15.

was quite satisfactory improvement for predictive value of $\overline{H}_1^E$ in all most systems and satisfactory improvement for $\overline{G}_1^E$ and $\overline{S}_1^E$ compared with original UNIFAC-FV. The excellent improvement for $\overline{H}_1^E$ was primarily due to prediction of the partial molar excess enthalpy through the estimation of parameters (A, B) by the linear least-squares analysis instead of fixing external degree of freedom (C_1) of original UNIFAC-FV as 1.1. The improvement for $\overline{G}_1^E$ and $\overline{S}_1^E$ was the same as the case of $\overline{H}_1^E$ except that $\overline{G}_1^E$ and $\overline{S}_1^E$ were subjective functions of $\overline{H}_1^E$ and activity coefficient in all systems. Furthermore, it was guessed that other factor of errors was the derivative of the free volume term of the UNIFAC-FV with temperature in the assumption that the liquid molar volumes of the UNIFAC-FV were constant in spite of the function of temperature [Elbro et al., 1991].

CONCLUSIONS

The activity coefficients were measured by an IGC method and extended to evaluate the partial molar excess properties of each solvent for the finitely concentrated solvent(1)/polymer(PMS, PVBC)(2) systems. The external degrees of freedom were obtained from experimental data to give flexibility to the original UNIFAC-FV model and its form became C_1=A+BT. The parameters were estimated by correlating the activities of each solvent in polymer solutions with the UNIFAC-FV model. The estimated parameters were again extended to predict the partial molar excess properties. The evaluated model could predict excellently the partial molar excess properties of each solvent in the finitely concentrated polymer solutions, that is, there was good agreement for $\overline{G}_1^E$ and $\overline{S}_1^E$ but a little error for $\overline{H}_1^E$.

ACKNOWLEDGMENT

The authors wish to acknowledge the financial support of the Korea Research Foundation made in the program of year 1997.

NOMENCLATURE

Table 4. Deviations between experimental and predicted values of partial molar excess properties by original UNIFAC-FV and revised UNIFAC-FV for solvent(1)/polymer(2) systems

Solvents	T (K)	w_1	$\overline{H}_1^E$		$\overline{G}_1^E$		$\overline{S}_1^E$	
			poly(4-methylstyrene)					
			UNIFAC-FV	This work	UNIFAC-FV	This work	UNIFAC-FV	This work
Acetone		0.0453-0.0633	66.32-76.69	8.65-15.21	33.31-41.30	8.82-14.91	0.23-0.29	0.00-0.03
n-Heptane		0.0115-0.0310	82.07-88.59	1.14-12.82	0.48-12.22	4.64-6.26	0.19-0.22	0.00-0.04
Cyclohexane		0.0176-0.0319	92.37-95.41	0.38-9.89	0.13-11.22	0.02-0.75	0.22-0.24	0.00-0.03
Chloroform		0.0350-0.0832	93.43-97.62	0.41-14.22	1.22-17.29	0.05-4.07	0.25-0.28	0.00-0.03
Methylisobutyl ketone	373.15-	0.0541-0.1444	56.47-87.27	0.46-23.04	0.54-8.05	0.04-1.29	0.15-0.23	0.00-0.09
Trichloroethylene	413.15	0.1200-0.1845	88.00-93.29	0.13-16.02	1.50-11.64	0.35-7.79	0.24-0.26	0.00-0.03
Benzene		0.0382-0.0600	-	1.44-22.17	0.08-9.27	0.65-6.87	0.29-0.30	0.00-0.08
Toluene		0.1003-0.2108	90.49-95.95	1.28-15.44	0.10-6.82	1.00-2.90	0.24-0.25	0.00-0.03
Ethylbenzene		0.1106-0.2501	-	0.04-21.60	0.83-14.45	0.87-3.54	0.24-0.25	0.01-0.52
Chlorobenzene		0.1941-0.3019	90.35-95.87	0.68-19.53	0.20-8.68	0.07-0.56	0.20-0.24	0.00-0.05
			poly(vinylbenzyl chloride)					
Acetone		0.0660-0.1048	94.62-96.37	5.13-18.08	19.04-30.48	5.69-21.15	0.32-0.33	0.01-0.03
n-Heptane		0.0198-0.0381	90.02-94.49	1.25-10.19	2.51-21.94	1.60-2.84	0.19-0.23	0.00-0.03
Cyclohexane		0.0228-0.0470	95.41-97.81	0.17-6.72	0.54-19.50	1.12-2.28	0.22-0.25	0.00-0.02
Chloroform		0.1054-0.1842	73.55-84.33	3.30-16.11	-	2.64-13.46	0.43-0.52	0.14-0.18
Methylisobutyl ketone	353.15-	0.2352-0.4153	-	0.10-9.93	0.57-10.67	0.30-0.92	0.26-0.27	0.00-0.03
Trichloroethylene	393.15	0.1259-0.2826	97.98-99.84	0.17-5.65	0.37-8.84	0.02-6.41	0.25-0.27	0.00-0.02
Benzene		0.0495-0.0699	96.47-98.97	0.94-9.34	0.47-10.60	0.55-1.31	0.26-0.28	0.00-0.03
Toluene		0.1933-0.3021	99.14-99.96	0.30-10.66	0.37-10.72	0.03-0.73	0.25-0.26	0.00-0.03
Ethylbenzene		0.2806-0.4098	99.10-99.79	0.79-13.82	5.02-17.13	0.01-0.30	0.23-0.24	0.00-0.04
Chlorobenzene		0.2731-0.4166	99.67- -	5.69-21.03	2.62-15.68	3.02-6.67	0.24-0.25	0.03-0.07

$$\text{Deviations (\%)} = \left|\frac{\text{Exp.data} - \text{Cal.value}}{\text{Exp.data}}\right| \times 100$$

A_1 : activity of component 1 based on weight fraction
a_{mn} : UNIFAC group interaction parameter between group m and n(K)
A, B : parameters on external degree of freedom
B_{11} : the 2^{nd} virial coefficient
b : proportionality factor of order unity (b=1.28)
C_1 : external degree of freedom of the component 1
C_s : concentration of solvent [mol·m^{-3}]
$\overline{G}_1^E$: partial molar excess Gibbs energy [J/mol]
$\overline{H}_1^E$: partial molar excess enthalpy [J/mol]
J : James-Martin factor
M_1, M_i, M_k : molecular weight of component 1, i and group k [g/mol]
m_2 : weight of polymer [g]
P_0, P_1, P_1^S : pressure of column output and solvent on stationary phase, saturated vapor pressure [kPa]
Q_{He} : flow rate of pure carrier gas at the column pressure [cm^3·s^{-1}]
q(p) : distribution isotherm of solvent at column pressure P [mol·g^{-1}]
q'_1, q'_i, q'_j : van der Waals surface area of component 1, i and j, respectively (per unit mass)
Q_k, Q'_k, Q'_m, Q'_n : molar group volume of group k and molar group volume of group k, m, n per unit mass respectively
R : gas constant [kPa·m^3/mol·K]
R_k, R'_k : molar group volume parameter and molar group volume parameter of group k per unit mass respectively
r'_1, r'_i, r'_j : van der Waals volume of component 1, i and j (per unit mass)
$\overline{S}_1^E$: partial molar excess entropy [J/mol·K]
T : experimental temperature [K]
T_F : flowmeter temperature [K]
t_S, t_a : retention time of solvent and air [s]
V_S, V_a : retention volume of solvent and air [cm^3]
v_1, v_2 : liquid molar volume of component 1, 2 [cm^3/g·mol]
$\tilde{v}_1$, $\tilde{v}_M$: reduced liquid molar volume of component i and polymer solution mixture, respectively
W_m, W_n : weight fraction of group m and n
w_1, w_2, w_i, w_j : weight fraction of component 1, 2, i and j
z : coordination number (z=10)

Greek Letters

A_1, A_1^c, A_1^R, A_1^{FV}: activity of component 1 (combinational term, residual term, free volume term based on weight fraction component 1)
Γ_k, $\Gamma_k^{(i)}$: activity coefficient of the group k and group k of pure component
Θ'_m, Θ'_n : surface area fraction of the group m and n
Ω_1^R, Ω_1^{FV} : activity coefficient of the component 1 (residual term and free volume term based on weight of component)
Ψ : true value of solvent vapor mole fraction on stationary phase

Ψ_{km}, Ψ_{nk}, Ψ_{nm} : interaction parameter of the group k, m and n
ϕ'_1, ϕ'_2, ϕ'_i : segment fraction of the component 1, 2 and i
$\nu_k^{(1)}$, $\nu_k^{(i)}$: number group of type k in molecule 1 and i
θ'_1, θ'_i : surface fraction of the component 1 and i

Superscripts

(1) : standard state (pure component)
4 : number of James-Martin factor
C : combinational
E : excess
FV : free volume
S : standard
R : residual
– : partial
~ : reduced

Subscripts

1, 2, i, j : molecule 1, 2, i and j
M : mixture
k, m, n : group k, m and n
P, w : constant pressure and weight fraction

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