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Inverse Gas Chromatography. 8. Apparent Probe Dependence of χ_{23}' for a Poly(vinyl chloride)−Poly(tetramethylene glycol) Blend

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ABSTRACT: Poly(vinyl chloride) (PVC), poly(tetramethylene glycol) (polytetrahydrofuran, PTHF), and their blend were studied at 120 °C by inverse gas chromatography (IGC). The retention behavior of the homopolymers and their blend (0.5 PTHF volume fraction) was characterized for 38 probes. The IGC-derived apparent polymer−polymer interaction parameters χ_{23}', ranging from −0.075 to 1.094, depended on the nature of the probe. The specific retention volumes V_g of the blend were found to be very close to the weight-average V_g values of PVC and PTHF suggesting a phase separation. The phase separation in the blend was confirmed by light scattering measurements. On the basis of the equation $V_{g,blend} = W_2V_{g,2} + W_3V_{g,3}$, an approximate expression, $\chi_{23}' = (\chi_{12} - \chi_{13})^2/2$, was obtained for phase-separated systems and was verified by IGC results for the PVC−PTHF blend. The apparent probe dependence of χ_{23}' for this system was well explained.

Introduction

The knowledge of the interaction parameter χ_{23} for a polymer−polymer pair is valuable in the study of polymer blend miscibility. Inverse gas chromatography (IGC) is one of the techniques useful for characterizing χ_{23}.[1] Because of its simplicity and rapid data collection, IGC has been used for many polymer systems.[2] However, as more studies were reported, the technique faced increasing doubts due to the strong dependence of the IGC-derived polymer−polymer interaction parameter χ_{23}' on the probe used.

Early in the development of the IGC technique the origin of the probe-dependence was traced to experimental artifacts and errors. From a careful study of the probe-dependence of χ_{23}' for the polymer pair poly(epichlorohydrin)−poly(methyl acrylate) Munk et al.[3] concluded that the probe dependence is real. Numerous attempts have been reported to resolve the problem of probe-dependent interaction parameters. DiPaola-Baranyi[4] proposed the possibility that nonrandom partitioning of probe molecules could affect the forces acting between molecules of the mixed stationary phases. Shi and Schreiber[5] attributed the probe dependence to the difference between the bulk and surface composition of the stationary phase. Klotz et al.[6] selected probes that were “thermodynamically symmetric” with respect to the polymers to be evaluated. El-Hibri, Cheng and Munk[7] found a correlation between the apparent $B_{23} = RT\chi_{23}'/V_1$ values and the Hildebrand solubility parameter of the probe. (V_1 is the molar volume of the probe.) Horta et al.[8] developed a modified form of Flory’s equation that allowed calculation of the probe-independent interaction parameter $\chi_{23}{*}^{T}$. His equation takes account of the equation-of-state parameters. Chee[9] calculated the polymer solubility parameter and the entropy contribution to the interaction parameter. Sanchez[10] suggested that full description of polymer mixture thermodynamics requires the definition of four different χ parameters. Chee and Deshpande[11] have proposed an interaction-density-parameter to overcome probe-to-probe variations in χ_{23}. Iruin[12,13] used an approach based on the lattice fluid theory in an attempt to eliminate the probe dependence of the thermodynamic parameters calculated by IGC.

The theoretical basis for the determinations of χ_{23}' by IGC is the Flory−Huggins expression for the change of free enthalpy in mixing, which is extended to three-component systems. Although this calculation of χ_{23}' is applicable only to homogeneous systems, it has been used frequently for phase-separated blends.[2,14] The ambiguous χ_{23}' thus derived was found to show a marked probe dependence.[11]

The present work attempts to understand the reason the interaction coefficient is apparently probe dependent for poly(vinyl chloride) (PVC), poly(tetramethylene glycol) (polytetrahydrofuran, PTHF) blends. The pair PVC−PTHF was selected, because only very weak specific interactions exist between constituents of the individual polymer chains. This may result in phase separation. To our knowledge, the miscibility of PVC−PTHF has not been characterized. Here 38 probes, representing a number of chemical group families, were used to facilitate the correlation of χ_{23}' values with the nature of the probe.

Theory

By combination of the Flory−Huggins theory with routine chromatographic calculations, the expression for the residual free energy parameter of binary interaction, χ_{12}, can be written as[15,7]

$$\chi_{12} = \ln(RTv_2/V_gV_1P^0_1) - 1 + V_1/M_2v_2 - (B_{11} - V_1)P^0_1/RT \quad (1)$$

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where V_1 and $P^0{}_1$ represent the probe molar volume in the liquid phase and saturated vapor pressure, respectively, B_{11} is the second virial coefficient of the probe in the gas phase, v_2 is the specific volume of the polymer at the experimental temperature, M_2 is the molecular weight of the polymer, R and T are the gas constant and absolute temperature, and V_g is specific retention volume of probe on the gas chromatographic column. When the IGC column contains a blend of two polymers, the system involves three components. For a ternary system, the Flory–Huggins expression for the free energy of mixing is frequently written as[16]

$$\Delta G_{\mathrm{mix}} = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + n_1\phi_2\chi_{12} + n_1\phi_3\chi_{13} + n_2\phi_3\chi_{23}] \qquad (2)$$

where ϕ_i and n_i are the volume fractions and the numbers of moles of the pertinent system components and the χ_{ij} values are the binary interaction parameters. Usually the subscript 1 is used to denote the probe, while the two polymers are denoted by 2 or 3.

The parameter χ_{23}' defined as

$$\chi_{23}' = (V_1/V_2)\chi_{23} \qquad (3)$$

is employed to characterize the binary interaction between the two polymers. Combination of the chromatographic theory with the derivative of eq 2 yields[3,7]

$$\chi_{23}' = (1/\phi_2\phi_3)\{\ln[V_{\mathrm{g,blend}}/(W_2v_2 + W_3v_3)] - \phi_2 \ln(V_{\mathrm{g},2}/v_2) - \phi_3 \ln(V_{\mathrm{g},3}/v_3)\} \qquad (4)$$

Here, the second subscript after V_g denotes the nature of the column and W_is are the weight fractions of the two components in the blend. Equation 4 is widely used in the routine IGC calculation of polymer–polymer interaction parameter.[2,3]

However, eqs 2 and 4 are applicable only to homogeneous systems. If the blend is phase-separated, $V_{\mathrm{g,blend}}$ is related to $V_{\mathrm{g},2}$ and $V_{\mathrm{g},3}$ as follows[17]

$$V_{\mathrm{g,blend}} = V_{\mathrm{g},2}W_2 + V_{\mathrm{g},3}W_3 \qquad (5)$$

By rearrangement of eq 1, $V_{\mathrm{g},2}$ and $V_{\mathrm{g},3}$ can be represented as

$$V_{\mathrm{g},i} = Kv_i \exp(-\chi_{1i}) \quad (i = 2, 3) \qquad (6)$$

where K can be a constant related only to the properties of the probe, because the term of V_1/M_iv_i in eq 1 may be omitted for most work involving high molecular weight polymers. Substitution of eq 6 into eq 5 yields

$$V_{\mathrm{g,blend}} = K[W_2v_2 \exp(-\chi_{12}) + W_3v_3 \exp(-\chi_{13})] \qquad (7)$$

Substituting eqs 6 and 7 into eq 4, we obtain

$$\chi_{23}' = \{\ln[\phi_2 \exp(-\chi_{12}) + \phi_3 \exp(-\chi_{13})] + \phi_2\chi_{12} + \phi_3\chi_{13}\}/\phi_2\phi_3 \qquad (8)$$

By expanding the function $\phi_2\phi_3\chi_{23}'$ into a Taylor series in two variables χ_{12} and χ_{13} (see Appendix) and retaining only the linear and quadratic terms, we find that the approximate value of χ_{23}' can be written as

$$\chi_{23}' = (\chi_{12} - \chi_{13})^2/2 \qquad (9)$$

It is obvious that for the phase separated systems the apparent interaction parameter χ_{23}' obtained by using eq 4 in routine IGC procedure is not realistic. The dependence of the apparent χ_{23}' on the properties of the probes is given by eq 9 in such a case.

Experimental Section

Materials. The PVC and PTHF samples used were purchased from Scientific Polymer Products. Molecular weights were 75000 and 2900, respectively. Specific volume of polymers were calculated from the density at 25 °C and the expansion coefficients which were available from the literature.[18] The specific volumes v_2 and v_3 thus derived for the two polymers at 120 °C were 0.7435 and 1.086 for PVC and PTHF, respectively. The chromatographic support was 60/80 mesh Chromosorb W, acid washed and treated with DCMS. All the probes were obtained from reputable suppliers and used as received. The vapor pressure of the probes was obtained from their Antoine vapor pressure coefficients; these coefficients together with other necessary constants were extracted from the Dreisbach compilation and other sources.[19,20]

Column Preparation. Packed columns were prepared out of 157-cm-long strips of $^1/_4$-in.-o.d. copper tubing. The polymer samples were first weighed carefully and dissolved in about 100 mL of tetrahydrofuran. The polymer samples were then deposited onto the support by employing a procedure described in an earlier work.[7] The column loading was 7%. Prior to any retention measurements each new column was conditioned in the chromatograph at 120 °C for 8 h. The two parent homopolymers and their blend (50/50 by volume) were studied.

Data Acquisition. A modified Varian Aerograph Model 2100 GC unit was utilized for gathering all the elution data. High-purity nitrogen was used as the carrier gas. The experiments were performed at 120 °C and at nominal flow rate of 16 mL/min. Methane served as a marker. A more detailed description of the apparatus is given in an earlier work.[7] During the data analysis, the correction for retention of marker and for retention by support have been performed as described earlier.[7,21]

Light-scattering measurements were performed to characterize the phase structure of PTHF/PVC blend at 120 °C. The sample for the light scattering measurement was prepared by solution casting from tetrahydrofuran**.** The measurements were conducted on our homemade time-resolved light scattering (TRLS) apparatus. The light source was a 15 mw plane-polarized He–Ne laser with a wavelength of 632.8 nm. The sample sandwiched between two cover glasses was inserted into a heating chamber kept at a constant temperature with an accuracy of ±0.1 °C. The chamber was set horizontally on the light-scattering stage. Radiation from the He–Ne gas laser was applied vertically to the specimen. The light scattering profile $I(q)$ (relative scattered intensity I vs scattering vector $\mathbf{q}$) under a V_v (parallel polarized) optical alignment was determined using a two-dimensional CCD-camera detector with 512 × 512 pixels and intensity resolution of 256 levels. The magnitude of the scattering vector $\mathbf{q}$, corresponding to the wavenumber of the concentration fluctuation, is defined by

$$q = (4\pi/\lambda) \sin(\theta/2) \qquad (10)$$

where θ is the scattering angle and λ the wavelength of the laser in the sample. The light scattering profile $I(q) \sim q$ was recorded at 120 °C. The phase structure parameters were obtained by the Debye–Bueche plot; i.e., by the plot of $I(q)^{-1/2}$ vs q^2.

Results and Discussion

The experimental values of the specific retention volumes V_g on PVC, PTHF, and their blend are listed in Table 1. The polymer probe interaction parameters χ_{12} and χ_{13} calculated from specific retention volumes by using eq 1, and the apparent polymer–polymer interaction parameters χ_{23}' calculated from eq 4 for 38

Table 1. Specific Retention Volumes, V_g, of Various Probes on PVC, PTHF, and Their Blend at 120 °C

no.[b]	probe	$V_{g,2}$	$V_{g,3}$	$V_{g,blend}$	$W_2V_{g,2} + W_3V_{g,3}$
1	pentane	1.524	7.051	3.743	3.771
2	hexane	2.643	13.173	6.923	6.922
3	heptane	4.470	24.373	12.672	12.558
4	octane	7.604	44.880	23.007	22.753
5	nonane	13.476	82.780	42.037	41.640
6	decane	23.407	151.682	76.026	75.537
7	undecane	40.536	277.746	136.989	136.937
8	cyclohexane	5.929	27.301	15.123	14.614
9	cycloheptane	15.631	68.197	37.700	36.994
10	cyclooctane	35.807	152.629	84.718	83.283
11	cyclohexene	9.839	35.749	20.458	20.369
12	cyclohexadiene	13.237	39.648	23.804	23.970
13	benzene	18.615	46.443	29.535	29.925
14	toluene	34.562	87.089	55.271	55.909
15	ethylbenzene	52.541	149.459	90.680	91.928
16	chlorobenzene	68.374	181.462	112.620	114.332
17	methyl chloride	2.064	5.168	3.260	3.326
18	methylene chloride	8.085	24.325	14.485	14.685
19	chloroform	11.370	47.938	25.891	26.231
20	carbon tetrachloride	9.040	37.131	20.648	20.456
21	butyl chloride	10.882	31.791	19.352	19.379
22	pentyl chloride	19.483	60.030	35.962	35.961
23	chlorohexane	47.309	132.793	82.694	82.049
24	chlorooctane	103.335	376.393	212.969	214.305
25	methylchloroform	9.436	35.934	20.505	20.205
26	1,1-dichloroethane	8.767	27.322	16.186	16.308
27	1,2-dichloroethane	20.611	53.884	33.857	34.133
28	trichloroethylene	17.295	58.489	33.666	34.036
29	tetrahydrofuran	17.522	31.201	22.851	23.081
30	dioxane	39.357	63.032	48.051	48.978
31	acetone	10.646	14.548	11.996	12.232
32	methyl ethyl ketone	18.455	27.660	21.972	22.196
33	methyl acetate	8.263	16.005	11.241	11.410
34	ethyl acetate	11.489	25.151	16.765	17.041
35	propyl acetate	20.102	45.444	30.074	30.401
36	*n*-butyl acetate	35.558	84.897	54.783	55.609
37	propanol	9.913	38.481	21.323	21.523
38	butanol	18.189	79.801	42.456	43.227

[a] Units of V_g are mL/g. [b] As employed in Table 2.

Table 2. PVC−PTHF Apparent Interaction Parameters χ_{23}', Along with the Probe−Polymer Binary Interaction Parameters at 120 °C

no.	probe	χ_{12}	χ_{13}	χ_{23}'
1	pentane	1.742	0.588	0.601
2	hexane	1.840	0.612	0.711
3	heptane	1.952	0.634	0.848
4	octane	2.055	0.657	0.950
5	nonane	2.114	0.675	0.992
6	decane	2.188	0.696	1.047
7	undecane	2.268	0.720	1.094
8	cyclohexane	1.540	0.390	0.763
9	cycloheptane	1.427	0.332	0.647
10	cyclooctane	1.389	0.317	0.617
11	cyclohexene	1.142	0.230	0.419
12	cyclohexadiene	0.844	0.125	0.225
13	benzene	0.541	0.004	0.089
14	toluene	0.558	0.011	0.101
15	ethylbenzene	0.703	0.035	0.164
16	chlorobenzene	0.494	−0.105	0.116
17	methyl chloride	0.598	0.059	0.064
18	methylene chloride	0.603	−0.120	0.201
19	chloroform	0.747	−0.314	0.485
20	carbon tetrachloride	1.111	0.076	0.550
21	butyl chloride	0.881	0.187	0.230
22	pentyl chloride	0.872	0.124	0.273
23	chlorohexane	0.646	−0.009	0.241
24	chlorooctane	1.127	0.212	0.379
25	methylchloroform	0.910	−0.049	0.502
26	1,1-dichloroethane	0.740	−0.018	0.251
27	1,2-dichloroethane	0.624	0.041	0.135
28	trichloroethylene	0.776	−0.064	0.299
29	tetrahydrofuran	0.265	0.067	−0.020
30	dioxane	0.414	0.321	−0.072
31	acetone	0.577	0.642	−0.075
32	methyl ethyl ketone	0.475	0.448	−0.040
33	methyl acetate	0.797	0.514	−0.019
34	ethyl acetate	0.786	0.380	0.016
35	propyl acetate	0.732	0.294	0.052
36	*n*-butyl acetate	0.730	0.237	0.060
37	propanol	1.599	0.621	0.423
38	butanol	1.507	0.406	0.505

[a] Probe = component 1; PVC = component 2; PTHF = component 3; (23) designates blend.

probes at 120 °C are given in Table 2. The precision of this method has been discussed before.[7] The variability of independent measurements for the same column has been reduced to better than 0.3%. From the definition of χ_{23}' this quantity should be expected to vary only mildly with the molar volume of the probe. However, from Table 2 it is quite clear that the χ_{23}' values exhibit a marked dependence on the probes. This is a major problem encountered often with the IGC method. The probes used here have been carefully selected to span a wide range of polarities. By inspecting Table 2, one finds that large positive χ_{23}' values were obtained with probes for which the difference between χ_{12} and χ_{13} was large. On the other hand, by inspecting Table 1, one finds that the $V_{g,blend}$ is approximately equal to the weight-average values of $V_{g,2}$ and $V_{g,3}$. The quantity of $V_{g,blend}$ is plotted in Figure 1 for 38 probes against ($V_{g,2}W_2 + V_{g,3}W_3$). As is apparent from Figure 1, most of the data points are on the diagonal, which suggests that eq 5 is valid for the PVC−PTHF blends.

According to the literature,[17] when a phase-separated blend is used in IGC, $V_{g,blend}$ is equal to the theoretical value of the weight-average V_g values of the pure components. Consequently, Figure 1 and the data of Table 2 suggest that the PVC−PTHF blends are probably phase separated.

The Debye−Bueche plot obtained from the light scattering measurement at 120 °C is shown in Figure 2. In the range of q^2 smaller than 3 μm^{-2}, the plot is a straight line. According to the Debye−Bueche equation[23]

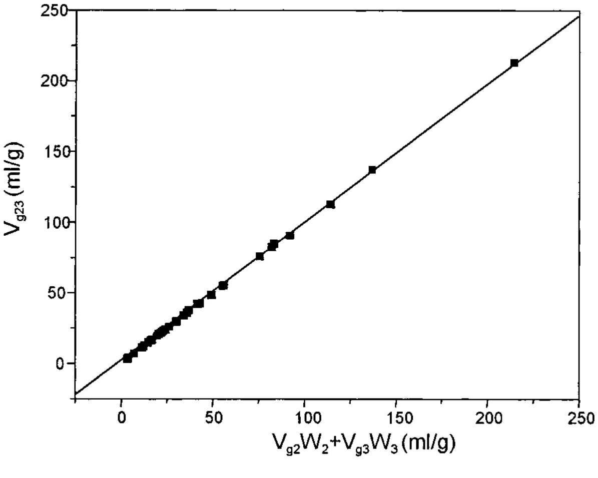

Figure 1. Specific retention volumes $V_{g,23}$ of PVC−PTHF blend for 38 probes plotted against ($V_{g,2}W_2 + V_{g,3}W_3$).

$$I(q)^{-1/2} = [(8\pi \langle\eta^2\rangle\xi^3)^{-1/2}](1 + \xi^2q^2) \qquad (11)$$

where $\langle\eta^2\rangle$ is the mean-square fluctuation of refractive index and ξ is the correlation length of the phase

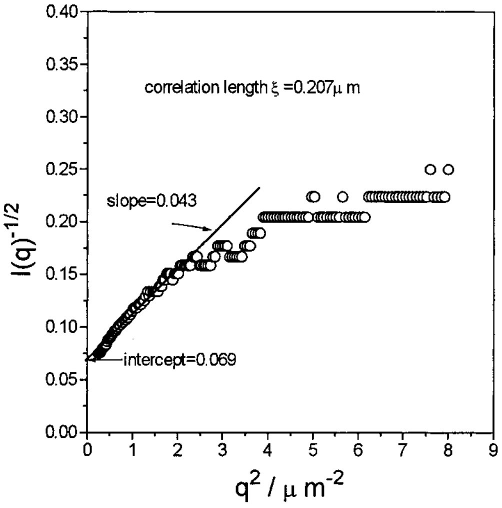

Figure 2. Debye−Bueche plot for 50/50 PTHF/PVC blend at 120 °C.

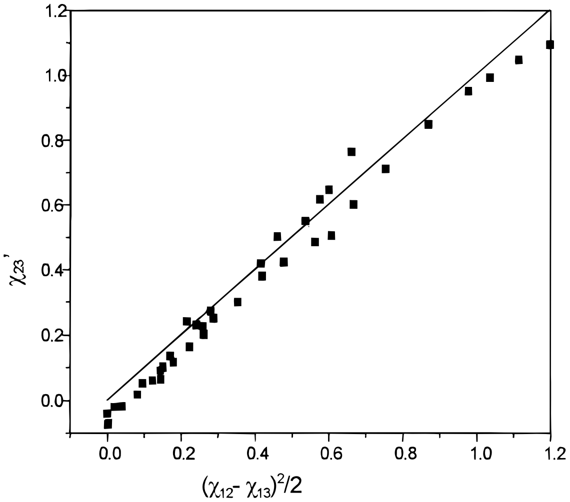

Figure 3. Apparent PVC−PTHF interaction parameters χ_{23}' plotted against $(\chi_{12} - \chi_{13})^2/2$ for 38 probes.

structure in the blend. From this plot, the correlation length ξ can be obtained from the slope and the intercept at the $I(q)^{-1/2}$ axis. The value $\xi = 207$ nm was found for the 50/50 PTHF/PVC blend at 120 °C. The mean radius $\bar{R}$ of the domain can be calculated by

$$\bar{R} = 3\xi/(4(1 - \phi)) \tag{12}$$

where ϕ is the volume fraction of the dispersed phase. $\bar{R} = 310$ nm is thus obtained. The scattered light at large q is attributed to the small size particles. The intensity at large q is very low, which indicates the low concentration of small size particles; therefore, the change of scattered light intensity with q at large q apparently cannot be measured by the present instrument. However, this will not affect the results of the determination of the mean particle size by weight a great deal, because the concentration of small size particles is so low. Hence, light scattering measurements do demonstrate that phase separation exists in the system of PTHF/PVC blend at 120 °C.

The χ_{23}' values are shown in Figure 3 plotted against $(\chi_{12} - \chi_{13})^2$ / 2 for the 38 probes studied. With the exception of very few probes, the data-points are around the diagonal. Figure 3 verified eq 9 and revealed an extensive correlation between χ_{23}' values and probe characteristics for the phase-separated blend systems.

The failure of the traditional approach of the evaluation of χ_{23}' for phase-separated systems is due to the fact that eq 2 is applicable only to homogeneous systems. When a phase-separated blend is used in IGC, χ_{23}' values obtained from eq 4 are unrealistic. These χ_{23}' values should depend on the probe characteristics in the manner predicted by eq 9.

The approach offered here is successful in limited case, but broader analyses are still needed to account for analogous problems in miscible polymer blends where the problem of probe-dependence is much more complicated.[3] Nevertheless, it was often observed with some miscible blends[22] that the larger was the difference between χ_{12} and χ_{23}, the bigger positive χ_{23}' values were obtained. It perhaps implies that the homogeneous mixtures of polymers on the molecular scale were not formed in these systems.

According to eq 9, χ_{23}' values should be always positive, but the data of Table 2 show that the strongly polar probes such as acetone, dioxane and methyl acetate gave negative χ_{23}' values. Although very close to zero, these negative χ_{23}' values are believed not to arise from experimental error. In our view, the deviation from eq 11 comes from the weak special interaction on the interface of two polymers in the PVC−PTHF blend.

Conclusions

For phase-separated blend systems the polymer−polymer interaction parameter χ_{23}' values calculated from eq 2 and eq 5 are unrealistic. An approximate equation $\chi_{23}' = (\chi_{12} - \chi_{13})^2/2$, derived in this paper, is able to explain the probe-dependence of the apparent interaction parameter χ_{23}'. This equation was verified by IGC results of PVC−PTHF blend.

Appendix

Equation 8 can be simplified to

$$X = \ln(\phi_2 e^{-\chi_{12}} + \phi_3 e^{-\chi_{13}}) + \phi_2\chi_{12} + \phi_3\chi_{13}$$

where

$$X = \phi_2\phi_3\chi_{23}'$$

Because both χ_{12} and χ_{13} are close to zero, by expanding the function X in a Taylor's series in two variables we obtain

$$X(\chi_{12}\chi_{13}) \approx X(0,0) + \chi_{12}\frac{\partial X(0,0)}{\partial\chi_{12}} + \chi_{13}\frac{\partial X(0,0)}{\partial\chi_{13}} + \frac{1}{2}\left[{\chi_{12}}^2\frac{\partial^2 X(0,0)}{\partial{\chi_{12}}^2} + {\chi_{13}}^2\frac{\partial^2 X(0,0)}{\partial{\chi_{13}}^2} + 2\chi_{12}\chi_{13}\frac{\partial^2 X(0,0)}{\partial\chi_{12}\partial\chi_{13}}\right] \tag{A.1}$$

where

$$\frac{\partial X}{\partial\chi_{12}} = \frac{\phi_2 e^{-\chi_{12}}(-1)}{\phi_2 e^{-\chi_{12}} + \phi_3 e^{-\chi_{13}}} + \phi_2$$

$$\frac{\partial X}{\partial\chi_{3}} = \frac{\phi_3 e^{-\chi_{13}}(-1)}{\phi_2 e^{-\chi_{12}} + \phi_3 e^{-\chi_{13}}} + \phi_3$$

$$\frac{\partial X(0,0)}{\partial \chi_{12}} = 0$$

$$\frac{\partial X(0,0)}{\partial \chi_{13}} = 0$$

$$\frac{\partial^2 X}{\partial {\chi_{12}}^2} = \frac{\phi_2 e^{-\chi_{12}}(-1)(\phi_2 e^{-\chi_{12}} + \phi_2 e^{-\chi_{13}})(-1) - \phi_2 e^{-\chi_{12}}(-1)\phi_2 e^{-\chi_{12}}(-1)}{(\phi_2 e^{-\chi_{12}} + \phi_3 e^{-\chi_{13}})^2} = \frac{\phi_2\phi_3 e^{-\chi_{12}} e^{-\chi_{13}}}{(\phi_2 e^{-\chi_{12}} + \phi_3 e^{-\chi_{13}})^2}$$

$$\frac{\partial^2 X}{\partial {\chi_{13}}^2} = \frac{\phi_2\phi_3 e^{-\chi_{12}} e^{-\chi_{13}}}{(\phi_2 e^{-\chi_{12}} + \phi_3 e^{-\chi_{13}})^2}$$

$$\frac{\partial^2 X}{\partial \chi_{12}\chi_{13}} = \frac{-\phi_2\phi_3 e^{-\chi_{12}} e^{-\chi_{13}}}{(\phi_2 e^{-\chi_{12}} + \phi_3 e^{-\chi_{13}})^2}$$

$$\frac{\partial^2 X(0,0)}{\partial {\chi_{12}}^2} = \phi_2\phi_3$$

$$\frac{\partial^2 X(0,0)}{\partial {\chi_{13}}^2} = \phi_2\phi_3$$

$$\frac{\partial^2 X(0,0)}{\partial \chi_{12}\chi_{13}} = -\phi_2\phi_3$$

Equation A.1 results in

$$X(\chi_{12}\chi_{13}) \approx \frac{1}{2}\phi_2\phi_3[{\chi_{12}}^2 + {\chi_{13}}^2 - 2\chi_{12}\chi_{13}] = \frac{1}{2}\phi_2\phi_3[\chi_{12} - \chi_{13}]^2$$

$$\chi_{23}' \approx \frac{1}{2}[\chi_{12} - \chi_{13}]^2$$

References and Notes

(1) Deshpande, D. D.; Patterson, D.; Schreiber, H. P.; Su, C. S. *Macromolecules* **1974**, *7*, 530.
(2) Mandal, B. M.; Bhattacharya, C.; Bhattacharyya, S. N. *J. Macromol. Sci.-Chem.* **1989**, A26, 175.
(3) Al-Saigh, Z. Y.; Munk, P. *Macromolecules* **1984**, *17*, 803.
(4) DiPaola-Baranyi, G.; Degre, P. *Macromolecules* **1981**, *17*, 63.
(5) Shi, Z. H.; Schreiber, H. P. *Macromolecules* **1991**, *24*, 3522.
(6) Klotz, S.; Grater, H.; Canton, H. J. In *Inverse Gas Chromatography*; Lloyd, D. R., Ward, T. C., Schreiber, H. P., Eds.; ACS Symposium Series 391; American Chemical Society: Washington DC, 1989.
(7) El-Hibri, M. J.; Cheng, W.; Munk, P. *Macromolecules* **1988**, *21*, 3458.
(8) Prolongo, M. G.; Masegosa, R. M.; Horta, A. *Macromolecules* **1989**, *22*, 4346.
(9) Chee, K. K. *Polymer* **1990**, *31*, 1711.
(10) Sanchez, I. C. *Polymer* **1989**, *30*, 471.
(11) . Farooque, A. M.; Deshpande, D. D. *Polymer* **1992**, *33*, 23.
(12) Etxeberria, A.; Uriarte, C.; Iruin, J. J. *Macromolecules* **1994**, *27*, 1245
(13) Etxeberria, A.; Iriarte, M.; Uriarte, C.; Iruin, J. J. *Macromolecules* **1995**, *28*, 7188.
(14) Tripathi, V. S.; Lal, D.; Sen, A. K. *J. Appl. Polym. Sci.* **1995**, *58*, 1681.
(15) Lavoie, A.; Guillet, J. E. *Macromolecules* **1969**, *2*, 443.
(16) Scott, R. L. *J. Chem. Phys.* **1949**, *17*, 268.
(17) Zhikuan, C.; Walsh, D. J. *Eur. Polym. J.* **1983**, *19*, 519.
(18) van Krevelen, D. W. In *Properties of Polymers*; Elsevier: Amsterdam, 1972.
(19) Dreisbach, R. R. *Adv. Chem. Ser.* **1955**, *No. 15*; **1959**, *No. 22*; **1961**, *No. 29*.
(20) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. In *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.
(21) El-Hibri, M. J.; Munk, P. *Macromolecules* **1988**, *21*, 264.
(22) Su, S. S.; Paterson, D. *Macromolecules* **1977**, *10*, 708.
(23) Debye, P. and Bueche, A. M. *J. Appl. Phys.* **1949**, *20*, 518.

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