

# Thermodynamics of Polymer–Polymer–Solvent and Block Copolymer–Solvent Systems

## II. Theoretical Treatment of Data with the Nonrandom New Flory Theory

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**ABSTRACT:** Experimental data previously reported<sup>1</sup> are treated with the nonrandom new Flory theory of polymer solutions. The theory is applied to polymer–polymer–solvent systems and extended to the block copolymer–solvent case. Polymer–polymer binary interaction parameters are determined. Equations for  $\chi$  interaction parameters are identical in form for the polymer–solvent, polymer–polymer–solvent and block copolymer–solvent case. The ability of the theory to fit the experimental data is satisfactory.

**KEY WORDS** Polymer Mixtures / Block Copolymers / New Flory Theory / Nonrandom Mixing /

Most of the reported polymer pairs<sup>2,3</sup> showing an appreciable degree of compatibility are by no means simple nonpolar molecules. Specific interactions imply a certain degree of nonrandomness in molecular arrangements in the mixture, although they are not, probably, the only cause for nonrandom arrangements in liquids and their mixtures. Orientational order has been observed even in *n*-alkane liquids.<sup>4</sup> The need for corrections for nonrandomness was suspected several times in the past<sup>5–7</sup> partly as a cause of discrepancies between theoretical and experimental results.

In this work, we treat the experimental data reported previously<sup>1</sup> with the equation of state theory of Flory and coworkers<sup>8</sup> corrected for nonrandomness. The correction for nonrandomness follows closely the lines of our previous work.<sup>7,9</sup> Working equations are presented for ternary systems and the theory is extended to include the solvent–block copolymer case. The new Flory theory<sup>8</sup> has been

chosen because of its simplicity and the fact that the pure component equation of state parameters are frequently available in the literature.

### POLYMER–POLYMER–SOLVENT CASE

The configurational partition function (the other factors of the partition function are of no concern to us here) in its maximum term approximation may be written as<sup>8,9</sup>

$$Q_N = g_c g_{NR} \psi^N \exp(-E_0/RT) \quad (1)$$

where  $g_c$  is the combinatorial contribution accounting for the number of distinguishable random arrangements of the molecules in the system;  $g_{NR}$  is a correction to  $g_c$  for nonrandom arrangements.  $\psi$  is the “cell” partition function or otherwise the “free volume” contribution of each of the  $N$  molecules;  $E_0$  is the mean intermolecular (attractive) energy of the system;  $R$ , gas constant and  $T$ , the

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temperature.

For simplicity, we keep for  $g_c$  the approximation of Flory<sup>10</sup> for a system of  $N_1$  monomers,  $\dots$ ,  $N_i r_i$ -mers, namely

$$g_c = \frac{(rN)!}{\prod_i N_i!} \left( \frac{Z-1}{rN} \right)^{N(r-1)} \quad (2)$$

where

$$rN = \sum_i N_i r_i \quad (3)$$

and

$$N = \sum_i N_i \quad (4)$$

The quasi-lattice coordination number  $Z$  has been arbitrarily set equal to ten.

For the free volume term, we assume

$$\psi = [\gamma v^*(\bar{v}^{1/3} - 1)^3]^{rc} \quad (5)$$

with

$$rc = \sum \phi_i r_i c_i \quad (6)$$

$3r_i c_i$  are the equivalent number of external degrees of freedom per  $r_i$ -mer in the Prigogine<sup>11</sup> sense.

If  $N_{ij}$  is the total number of  $i$ - $j$  contact pairs in the system then, in the van der Waals-type energy interaction form the intermolecular energy of the system may be written as

$$-E_0 = \sum_{j \geq i} \frac{N_{ij} \epsilon_{ij}}{v} \quad (7)$$

where  $\epsilon_{ij}$  is an interactional constant characteristic of pair  $i$ - $j$ .

The quasi-chemical<sup>12</sup> correction for non-randomness may be written as:

$$g_{NR} = \frac{\prod_i N_{ii}^0! \prod_{j \geq i} \left[ \frac{N_{ij}^0}{2} \right]^2}{\sum_i N_{ii}! \prod_{j \geq i} \left[ \frac{N_{ij}!}{2} \right]^2} \quad (8)$$

where superscript 0 indicates random values of  $N_{ij}$ 's.

The segment fraction is defined as

$$\phi_i = \frac{N_i r_i}{\sum_j N_j r_j} \quad (9)$$

For an  $r_i$ -mer it is assumed that the number of intermolecular contacts in which molecule  $i$  participates is given by<sup>12</sup>

$$Zq_i = (Z-2)r_i + 2 \quad (10)$$

The surface fraction  $\theta_i$  is given by

$$\theta_i = \frac{N_i Z q_i}{N Z q} \quad (11)$$

where

$$N Z q = \sum_i N_i Z q_i \quad (12)$$

Due to nonrandom arrangements, the local surface fractions  $\theta_{ij}$  are different from the overall surface fractions given by eq 11. Thus, the total number of  $i$ - $i$  contacts is approximated as

$$N_{ii} = \frac{N_i Z q_i}{2} \theta_{ii} \quad (13)$$

and, similarly, for  $i$ - $j$  contacts

$$N_{ij} = N_i Z q_i \theta_{ji} = N_j Z q_j \theta_{ij} \quad (14)$$

$\theta_{ii}$  is the fraction of nearest neighbors of type  $i$  around a central segment of type  $i$  and  $\theta_{ij}$  is the fraction of nearest neighbors of type  $i$  around a central segment of type  $j$ . The factor 1/2 in eq 13 is necessary in order to account for the symmetry of the arrangement  $i$ - $i$ . In terms of nonrandom factors, the above local surface fractions may be written as

$$\theta_{ii} = \theta_i \Gamma_{ii} \quad (15a)$$

$$\theta_{ij} = \theta_i \Gamma_{ij} \quad (15b)$$

$$\theta_{ji} = \theta_j \Gamma_{ij} \quad (15c)$$

In contrast to  $\theta_{ij}$ 's the nonrandom factors  $\Gamma_{ij}$ 's have no directional character ( $\Gamma_{ij} = \Gamma_{ji}$ ).

Following Guggenheim's quasi-chemical treatment,<sup>12</sup> the values of the  $N_{ij}$ 's ( $i \neq j$ ) are those that minimize the free energy of the system, leading to the quasi-chemical

conditions<sup>9</sup>

$$\frac{\theta_{ii}\theta_{jj}}{\theta_{ij}\theta_{ji}} = \exp \frac{\varepsilon_{ii} + \varepsilon_{jj} - 2\varepsilon_{ij}}{vRT} = G_{ij} \quad (16)$$

In the case of ternary systems, there are three quasi-chemical conditions, eq 16. In terms of local surface area fractions, the energy term  $-E_0$  may be written for the ternary case as:

$$\begin{aligned} -E_0 = & \frac{Nrv^*}{v} (\phi_1 P_1^* + \phi_2 P_2^* + \phi_3 P_3^* \\ & - \phi_1 \theta_{21} X_{12} - \phi_2 \theta_{32} X_{23} - \phi_3 \theta_{13} X_{31}) \end{aligned} \quad (17)$$

where

$$P_i^* = \frac{Zq_i}{2r_i} \frac{\varepsilon_{ii}}{v^{*2}} \quad (18)$$

and

$$X_{ij} = \frac{Zq_i}{2r_i} \frac{\varepsilon_{ii} + \varepsilon_{jj} - 2\varepsilon_{ij}}{v^{*2}} \quad (i \neq j) \quad (19)$$

The characteristic pressure,  $P^*$ , of the system is then given by

$$\begin{aligned} P^* = & \phi_1 P_1^* + \phi_2 P_2^* + \phi_3 P_3^* - \phi_1 \theta_{21} X_{12} \\ & - \phi_2 \theta_{32} X_{23} - \phi_3 \theta_{13} X_{31} \end{aligned} \quad (20)$$

while the characteristic temperature  $T^*$  is obtained from the relation

$$P^* v^* = cRT^* \quad (21)$$

Each of the three nonrandom factors  $\Gamma_{ij}$  ( $i \neq j$ ) is given by a relation of the form

$$\Gamma_{ij} = \frac{2(1 - 2\lambda\theta_i)}{(1 - 2\theta_i) + [(1 - 2\theta_i)^2 - 4(1 - G_{ij})\theta_i\theta_j(1 - 2\lambda\theta_i)]^{1/2}} \quad (i \neq j \neq t) \quad (22)$$

Details for the computation of the  $\Gamma_{ij}$ 's have been given previously.<sup>9</sup>

With the above definitions, the equation of state in terms of reduced variables has the form<sup>8</sup>

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{v}\tilde{T}} \quad (23)$$

where

$$\tilde{P} = \frac{P}{P^*} \quad (24)$$

and

$$\tilde{T} = \frac{T}{T^*} \quad (25)$$

The chemical potential is obtained from

$$\mu_1 = \left( \frac{\partial \ln Q_N}{\partial N_1} \right)_{T, V, N_{j \neq 1}} \quad (26)$$

The activity  $a_1$  of component 1 is then given by:

$$\begin{aligned} \ln a_1 = & \frac{\mu_1 - \mu_1^0}{RT} \\ = & \ln \phi_1 + \left(1 - \frac{r_1}{r_2}\right) \phi_2 + \left(1 - \frac{r_1}{r_3}\right) \phi_3 \\ & + \frac{P_1^* r_1 v^*}{RT} \left[ 3\tilde{T}_1 \ln \frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} \right. \\ & \left. + \left( \frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}} \right) \right] + \frac{Zq_1}{2} \ln \Gamma_{11} \end{aligned} \quad (27)$$

Comparison of eq 27 with eq 8 of ref 1 gives for the  $\chi_{1,23}$  parameters with  $\phi_{23} = \phi_2 + \phi_3$

$$\begin{aligned} \chi_{1,23} = & \frac{1}{\phi_{23}^2} \left\{ \frac{Zq_1}{2} \ln \Gamma_{11} + \frac{P_1^* r_1 v^*}{RT} \right. \\ & \left. \times \left[ 3\tilde{T}_1 \ln \frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \left( \frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}} \right) \right] \right\} \end{aligned} \quad (28)$$

In the random case (zeroth approximation) the first term in eq 28 should be replaced by

$$\begin{aligned} \frac{v^*}{\tilde{v}RT\phi_{23}^2} \left( r_1 X_{12} \theta_2 (1 - \theta_1) + r_1 X_{13} \theta_3 (1 - \theta_1) \right. \\ \left. - \frac{Zq_1}{Zq_2} r_2 X_{23} \theta_2 \theta_3 \right) \end{aligned}$$

Equation 28 is valid for binaries as well.<sup>9</sup>

The treatment of polymer-polymer-solvent systems with the above formulation involves the following three steps:

—Determination of the  $X_{12}$  parameter from data on the Flory-Huggins  $\chi_{12}$  interaction

**Table I.** Equation of state parameters for pure components

Pure component	$P^*$	$T^*$	$v_{sp}^*$	Reference
	atm	K	cm <sup>3</sup> g <sup>-1</sup>	
Benzene (25°C)	6194	4709	0.8860	13
Benzene (58°C)	6054	4829	0.8948	14
Polystyrene	5395	7420	0.8100	15
Poly(vinyl methyl ether)	5390	7201	0.8284	16
<i>n</i> -Pentane	4010	4158	1.1828	17
Polyisobutylene	4418	7580	0.9493	17
<i>n</i> -Heptadecane	4418	5760	1.063	8
Chloroform	6274	4450	0.5124	7
Poly(vinyl chloride)	8645	7960	0.6240	18
Poly( $\epsilon$ -caprolactone)	5905	6363	0.769	18
Carbon tetrachloride	5586	4700	0.487	18
Poly(ethylene oxide)	6628	6469	0.7532	14
<i>n</i> -Tetracosane	4542	6020	1.0544	8

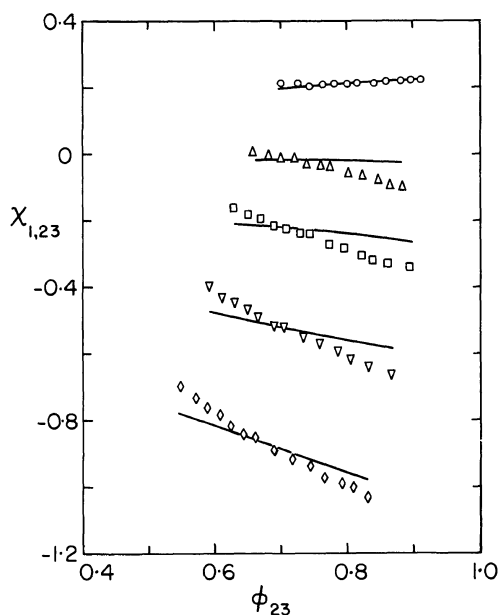
parameter for the system: solvent-polymer 2.

—Determination of the  $X_{13}$  parameter from data on the Flory-Huggins  $\chi_{13}$  interaction parameter for the system: solvent-polymer 3.

—Use of  $X_{12}$  and  $X_{13}$  for the determination of  $X_{23}$  parameter from data on  $\chi_{1,23}$  parameter for the system: solvent-polymer 2-polymer 3.

The pure component equation of state parameters are presented in Table I. Although the pure component parameters may change with temperature, the limited information available does not allow to consider this effect. In Figure 1 experimental and calculated values of the  $\chi_{1,23}$  parameter are presented for the system chloroform (1)-polystyrene (2)-poly(vinyl methyl ether) (3) at 25°C. The density of chloroform at 25°C is<sup>19</sup> 1.4794 g cm<sup>-3</sup>. The values of  $X_{ij}$  parameters for this system are:  $X_{12} = -2.27$  cal cm<sup>-3</sup>,  $X_{13} = -16.19$  cal cm<sup>-3</sup>,  $X_{23} = 0.015$  cal cm<sup>-3</sup>. No substantial improvement has been found by introducing a second parameter with the treatment as suggested previously.<sup>9</sup>

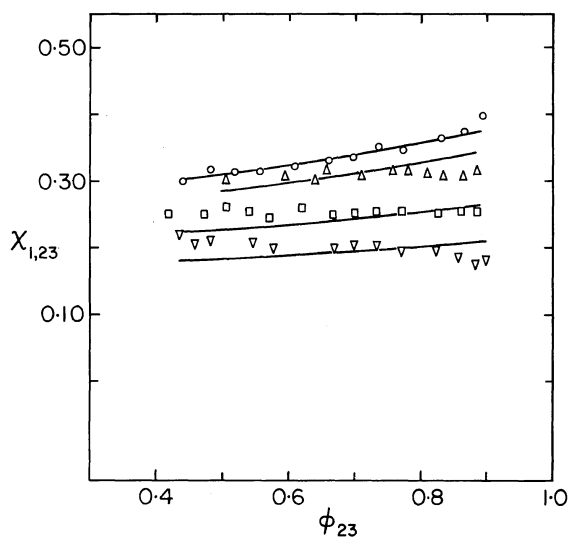
In Figure 2, experimental and calculated



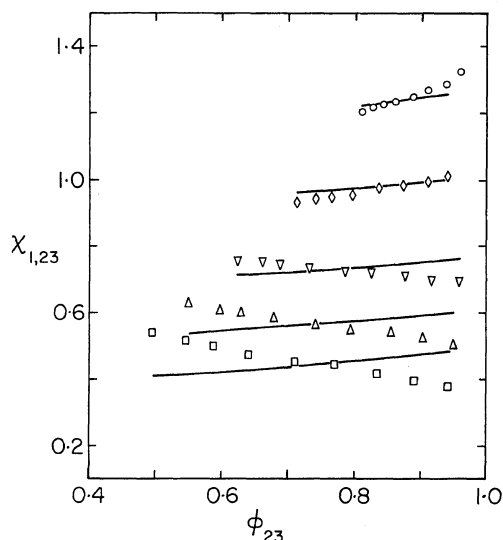
**Figure 1.** Experimental and calculated  $\chi_{1,23}$  parameters versus polymer mixture segment fraction  $\phi_{23}$  for the system chloroform (1)-polystyrene (2)-poly(vinyl methyl ether) (3) at 25°C. —, calculated; experimental points ( $w_{2p}$ ):  $\circ$ , 1.0;  $\triangle$ , 0.8012;  $\square$ , 0.6023;  $\nabla$ , 0.3337;  $\diamond$ , 0.0.

values of the  $\chi_{1,23}$  parameter are presented for the system benzene (1)-polystyrene (2)-poly(vinyl methyl ether) (3) at 25°C. The specific volume of benzene at 25°C is<sup>13</sup> 1.1444 cm<sup>3</sup> g<sup>-1</sup>. The values of the  $X_{ij}$  parameters for this system are:  $X_{12} = 0.13$  cal cm<sup>-3</sup>,  $X_{13} = -1.20$  cal cm<sup>-3</sup>,  $X_{23} = 0.019$  cal cm<sup>-3</sup>. Once again, no substantial improvement has been found by using a second parameter. The interesting result is the surprising good agreement in the  $X_{23}$  parameter obtained from data using two different probes. A minor difference in  $X_{23}$ 's arising from the different size of the two probes, as indicated by the defining eq 19, is always expected.

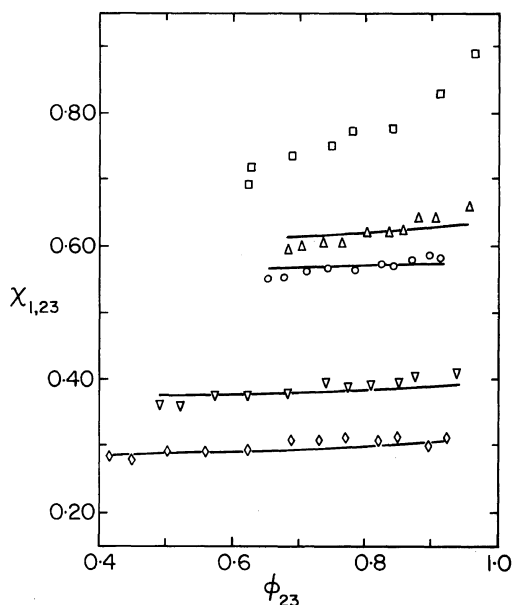
In Figure 3, experimental and calculated values of the  $\chi_{1,23}$  parameter are presented for the system carbon tetrachloride (1)-poly(vinyl chloride) (2)-poly( $\epsilon$ -caprolactone) (3) at 65°C. The specific volume of carbon tetrachloride is



**Figure 2.** Experimental and calculated  $\chi_{1,23}$  parameters versus polymer mixture segment fraction  $\phi_{23}$  for the system benzene (1)-polystyrene (2)-poly(vinyl methyl ether) (3) at 25°C. —, calculated; experimental points ( $w_{2p}$ ):  $\circ$ , 1.0;  $\triangle$ , 0.8012;  $\square$ , 0.3337;  $\nabla$ , 0.0.



**Figure 3.** Experimental and calculated  $\chi_{1,23}$  parameters versus polymer mixture segment fraction  $\phi_{23}$  for the system carbon tetrachloride (1)-poly(vinyl chloride) (2)-poly( $\epsilon$ -caprolactone) (3) at 65°C. —, calculated; experimental points ( $w_{2p}$ ):  $\circ$ , 1.0;  $\diamond$ , 0.7653;  $\nabla$ , 0.4784;  $\triangle$ , 0.2171;  $\square$ , 0.0.



**Figure 4.** Experimental and calculated  $\chi_{1,23}$  parameters versus polymer mixture segment fraction  $\phi_{23}$  for the system *n*-pentane (1)-polyisobutylene (2)-*n*-heptadecane (3) at 25°C. —, calculated; experimental:  $\square$ , *n*-pentane-polyisobutylene molecular weight 40000<sup>17</sup>;  $\triangle$ , *n*-pentane-polyisobutylene molecular weight 2700;  $\circ$ , *n*-pentane-polyisobutylene molecular weight 1350;  $\nabla$ , *n*-pentane-polymer mixture,  $w_{2p}=0.3854$ ;  $\diamond$ , *n*-pentane-*n*-heptadecane.

taken as<sup>20</sup>  $0.6639 \text{ cm}^3 \text{ g}^{-1}$ . The values of the  $X_{ij}$  parameters for this system are  $X_{12}=7.99 \text{ cal cm}^{-3}$ ,  $X_{13}=3.32 \text{ cal cm}^{-3}$ ,  $X_{23}=1.59 \text{ cal cm}^{-3}$ . Olabisi,<sup>21</sup> from gas-liquid chromatography measurements, has calculated  $X_{23}$  at 120°C for this system to be  $2.2 \text{ cal cm}^{-3}$  (30% poly(vinyl chloride) per weight) and  $3.0 \text{ cal cm}^{-3}$  (50% poly(vinyl chloride)). In view of the difference in temperatures, the reported values in the two works may be considered in satisfactory agreement with each other.

In Figure 4, the experimental and calculated values of the  $\chi_{1,23}$  parameter are presented for the system: *n*-pentane (1)-polyisobutylene (2)-*n*-heptadecane (3) at 25°C. In the same figure data on  $\chi_{12}$  parameter for the system pentane-high molecular weight polyisobutylene<sup>17</sup> are presented for the sake of comparison. The specific volume of pentane at 25°C is<sup>17</sup>  $1.6094$

$\text{cm}^3 \text{g}^{-1}$ . The values of the  $X_{ij}$  parameters for this system are:  $X_{12} = -0.12 \text{ cal cm}^{-3}$ ,  $X_{13} = 0.83 \text{ cal cm}^{-3}$ ,  $X_{23} = -0.31 \text{ cal cm}^{-3}$ . The calculated line for the polyisobutylene sample of molecular weight 2700 was obtained with  $X_{12} = 0.49 \text{ cal cm}^{-3}$ . Discrepancies may be expected because of possible "end effects" in this range of molecular weights.

### BLOCK COPOLYMER-SOLVENT SYSTEM

In this section the nonrandom new Flory theory is extended to the case of block copolymer-solvent systems. The treatment is limited to the case of two different types of blocks containing units of types A and B. Each block may have any number of units of a single type and the larger the blocks the better the approximation of the model is likely to be.

In the following treatment subscript 1 indicates the solvent containing units S; subscript 2 indicates the block copolymer containing units A and B; subscript 3 indicates the model homopolymer containing only units A; subscript 4 indicates the model homopolymer containing only units B.  $r_{LM}$  is the number of units of type L in the molecule of type M. Thus, L may be S, A or B and M may be 1, 2, 3, or 4.

Following Flory's convention<sup>8</sup> the size of each unit (segment) will be set equal to the size of the solvent. For the solvent it will be set

$$r_1 = r_{S1} = 1 \quad (29)$$

with a total number of external contacts per molecule:

$$Zq_1 = Z \quad (30)$$

The total number of units in molecule 2 is

$$r_2 = r_{A2} + r_{B2} \quad (31)$$

With a corresponding number of external contacts

$$Zq_2 = (Z-2)r_2 + 2 \quad (32)$$

The number of external contacts in which units A of the molecule 2 are participating is

$$Zq_{A2} = (Z-2)r_{A2} + l \quad (33)$$

where  $l=0$  or 1 or 2 depending on how many times block of type A is an end block. The rest of the external contacts of molecule 2 are then

$$Zq_{B2} = Zq_2 - Zq_{A2} \quad (34)$$

The fraction of contact sites A on each copolymer molecule is

$$v_{A2} = \frac{Zq_{A2}}{Zq_2} \quad (35)$$

and similarly for contact sites B

$$v_{B2} = \frac{Zq_{B2}}{Zq_2} = 1 - v_{A2} \quad (36)$$

In the solvent-block copolymer system there are two types of molecular surface fractions, namely

$$\theta_1 = \frac{N_1 Zq_1}{N_1 Zq_1 + N_2 Zq_2} = \frac{N_1 Zq_1}{N Zq} \quad (37)$$

and

$$\theta_2 = \frac{N_2 Zq_2}{N Zq} = 1 - \theta_1 \quad (38)$$

The three types of unit surface fractions are

$$\Theta_A = \frac{N_2 Zq_{A2}}{N Zq} = \frac{N_2 Zq_2}{N Zq} v_{A2} = \theta_2 v_{A2} \quad (39)$$

$$\Theta_B = \frac{N_2 Zq_{B2}}{N Zq} = \frac{N_2 Zq_2}{N Zq} v_{B2} = \theta_2 v_{B2} \quad (40)$$

$$\Theta_S = \frac{N_1 Zq_1}{N Zq} = \theta_1 = 1 - \Theta_A - \Theta_B \quad (41)$$

If the total number of external contact pairs L-K in the system is  $N_{LK}$ , the local unit surface fractions are defined by the relations:

$$N_{AA} = \frac{N Zq}{2} \Theta_A \Theta_{AA} \quad (42)$$

$$N_{BB} = \frac{N Zq}{2} \Theta_B \Theta_{BB} \quad (43)$$

$$N_{SS} = \frac{NZq}{2} \Theta_S \Theta_{SS} \quad (44)$$

$$N_{AB} = NZq \Theta_A \Theta_{BA} = NZq \Theta_B \Theta_{AB} \quad (45)$$

$$N_{AS} = NZq \Theta_A \Theta_{SA} = NZq \Theta_S \Theta_{AS} \quad (46)$$

$$N_{BS} = NZq \Theta_B \Theta_{SB} = NZq \Theta_S \Theta_{BS} \quad (47)$$

From the principle of conservation of the external contacts,<sup>7</sup> the above definitions lead to the following relation:

$$\sum_L \Theta_{LK} = 1 \quad L, K = A, B, S \quad (48)$$

The nonrandom factors  $\Gamma_{LK}$  are defined in a manner analogous to that described in the first section. For example

$$\Theta_{AB} = \Theta_A \Gamma_{AB} \quad (49)$$

With the above nomenclature, the exponential term of the partition function may be written as:

$$-\frac{E_0}{vRT} = \frac{NZq}{2vRT} \left[ \sum_L \Theta_L \varepsilon_{LL} - \sum_L \sum'_{K \neq L} \Theta_L \Theta_{KL} \Delta \varepsilon_{LK} \right] \quad (50)$$

Where, in the sum  $\sum'$  each pair should be taken once, and

$$\Delta \varepsilon_{LK} = \varepsilon_{LL} + \varepsilon_{KK} - 2\varepsilon_{LK} \quad (L, K \text{ being } A \text{ or } B \text{ or } S) \quad (51)$$

The determination of the local unit fractions is done in exactly the same manner as it was done previously in the first section for the ternary case. Similarly the quasi-chemical conditions (eq 16), written in terms of local unit surface fractions, have the general form

$$\frac{\Theta_{AA} \Theta_{BB}}{\Theta_{AB} \Theta_{BA}} = \exp \frac{\Delta \varepsilon_{AB}}{vRT} = G_{AB} \quad (16a)$$

Equation 22 is modified in a similar manner. The segment fractions are given by eq 9 for the case of two components ( $i = 1, 2$ ). The characteristic equation of state parameters are defined by the relations

$$P^* v^{*2} = \frac{Zq}{2r} \left( \sum_L \Theta_L \varepsilon_{LL} - \sum_L \sum'_{K \neq L} \Theta_L \Theta_{KL} \Delta \varepsilon_{LK} \right) \quad (52)$$

where

$$Nr = N_1 r_1 + N_2 r_2 \quad (53)$$

Again,

$$P^* v^* = cRT^* \quad (54)$$

where now

$$c = \phi_1 c_1 + \phi_2 c_2 = \phi_1 c_1 + \phi_2 \left( \frac{r_{A2} c_3 + r_{B2} c_4}{r_2} \right) \quad (55)$$

The inherent assumption in eq 55 is that each unit has the same value for the Prigogine  $c$  parameter,<sup>11</sup> in both the homopolymer and in the block copolymer, which is likely to be true if the blocks are long enough.

With all these definitions the equation for the  $\chi_{12}$  interaction parameter takes the simple form

$$\chi_{12} = \frac{1}{\phi_2^2} \left\{ \frac{Zq_1}{2} \ln \Gamma_{SS} + \frac{P_1^* r_1 v^*}{RT} \times \left[ 3\tilde{T}_1 \ln \frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \left( \frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}} \right) \right] \right\} \quad (56)$$

which is formally identical to eq 28.

*Application to the System: Benzene- $\alpha$ , $\omega$ -Alcoxy Poly(ethylene oxide)*

Data previously reported<sup>1</sup> will be used to estimate the polyethylene (high  $n$ -alkane)-poly(ethylene oxide) interaction constant. Each unit of the end blocks ( $\text{CH}_3(\text{CH}_2)_{17}$ ) and ( $\text{CH}_3(\text{CH}_2)_{20}$ ) is assumed to behave as a similar unit in  $n$ -tetracosane, while each unit of the internal block is assumed to behave as a similar unit in the poly(ethylene oxide) E600M<sup>1</sup> sample. The reduced volume for benzene at 55°C is<sup>14,20</sup> 1.3282.

From the treatment of the data on benzene (S) E600M (A) system, the following values are obtained:

$$\varepsilon_{AS} = 166350 \text{ cal cm}^{-3} \quad \text{and}$$

$$X_{SA} = -0.75 \text{ cal cm}^{-3}$$

Similarly, for the system benzene (S)-*n*-tetracosane (B),

$$\varepsilon_{BS} = 132706 \text{ cal cm}^{-3} \quad \text{and}$$

$$X_{SB} = 6.03 \text{ cal cm}^{-3}$$

Using these binary parameters, the treatment of the data on benzene-block copolymer 18-45-18<sup>1</sup> gives

$$\varepsilon_{AB} = 160390 \text{ cal cm}^{-3} \quad \text{and}$$

$$X_{BA} = -3.84 \text{ cal cm}^{-3}$$

and, similarly, for the system benzene-block copolymer 21-45-21<sup>1</sup>

$$\varepsilon_{AB} = 160368 \text{ cal cm}^{-3} \quad \text{and}$$

$$X_{BA} = -3.23 \text{ cal cm}^{-3}$$

The surprisingly negative values for the  $X_{BA}$  parameter may be due to end effects. In order to test this hypothesis, each unit of the internal block has been simulated with a similar unit of the high molecular weight poly(ethylene oxide) molecule (see ref 1).

For this system, the following values have been obtained at 70°C:

$$\varepsilon_{AS} = 169134 \text{ cal cm}^{-3} \quad \text{and}$$

$$X_{SA} = 0.97 \text{ cal cm}^{-3}$$

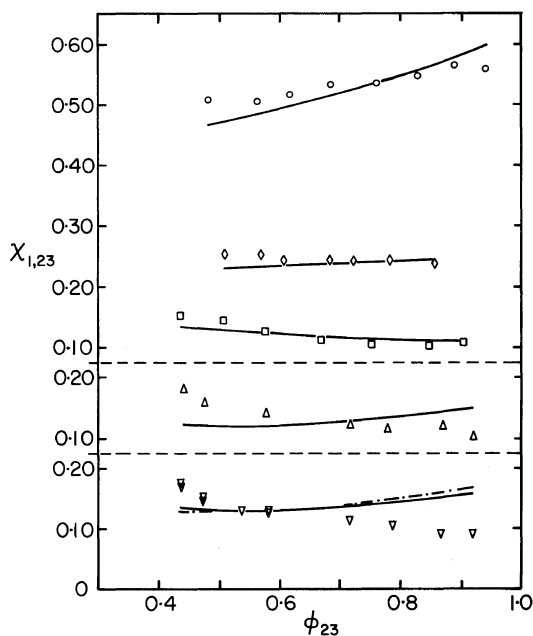
Using this parameter, the system benzene-(18-45-18) gave

$$\varepsilon_{AB} = 159395 \text{ cal cm}^{-3} \quad \text{and}$$

$$X_{BA} = 4.54 \text{ cal cm}^{-3}$$

which seem to be more reasonable values for this type of pair interaction.

In Figure 5 experimental and calculated data are presented for the solvent-copolymer systems and the corresponding solvent-homopolymer systems. In view of the several oversimplistic assumptions in this rather elementary theory, the results may be considered



**Figure 5.** Experimental and calculated  $\chi_{1,23}$  parameters versus polymer mixture segment fraction  $\phi_{23}$  for the system benzene (1)-poly(ethylene oxide) (2)-*n*-tetracosane (3). —, calculated with parameters at 55°C; ----, calculated with benzene-poly(ethylene oxide) parameters at 70°C; experimental: ○, benzene-*n*-tetracosane at 55°C; ◇, benzene-poly(ethylene oxide) molecular weight 100000 at 70°C; □, benzene-poly(ethylene oxide) molecular weight 600 at 55°C; △, benzene-copolymer 21-45-21 at 55°C; ▽, benzene-copolymer 18-45-18 at 55°C.

as gratifying.

## CONCLUSIONS

In this paper we have presented one of the many ways in which data on the Flory-Huggins  $\chi$  interaction parameters for ternary systems may be treated with the new Flory theory. To our knowledge this is the first attempt to treat this type of data (nonzero solvent concentration) with an equation of state approach. The introduction of the  $\chi_{1,23}$  parameter leads to a uniform treatment of ternary data for polymer solutions. Extension of the treatment to more than three components is straightforward. In this work only



one binary parameter ( $\varepsilon_{ij}$ ) has been used for fitting the data, although previous experience<sup>7</sup> has shown that just one parameter may not be enough for treating data on other thermodynamic functions of mixing such as heats of mixing and/or volumes of mixing. Due to the lack of more complete information, the binary parameters were determined using only data on  $\chi$  interaction parameters. Since this information may not be enough to give unique values of the binary parameters, the values of the parameters obtained in this work should be considered with caution. As for the fit of the data, before a final judgement is passed on the validity of the theory, the approximate nature of the pure component equation of state parameters of Table I should be considered, since variations of these parameters with temperature and molecular weight for oligomers and polymers have not been taken into account in this work. Probably one of the merits of this simple approach is its generality. More data and better pure component parameters are necessary to give a more definite judgement on the validity of the approach.

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## NOTATION

$a_1$	= activity of component 1 (solvent)
$E_0$	= mean intermolecular potential energy
$G_{ij}$	= binary constant defined by eq 16
$g_c$	= random combinatorial term
$g_{NR}$	= nonrandom combinatorial factor
$l$	= number indicating how many times a particular block is an end block
$N$	= number of moles
$N_{ij}$	= total number of external contacts of type $i-j$
$P$	= pressure
$Q_N$	= configurational partition function
$R$	= gas constant
$r$	= number of segments per molecule
$3rc$	= equivalent number of translational degrees of freedom per molecule
$T$	= temperature (K)
$v$	= volume per segment
$w_{2p}$	= weight fraction of component 2 in the polymer mixture

$x$	= mole fraction
$X_{ij}$	= binary parameter defined by eq 19
$Z$	= lattice coordination number
$Zq$	= number of external contacts per molecule

### Greek Letters

$\Gamma$	= nonrandom quasichemical factor
$\gamma$	= geometric factor in the cell partition function
$\Delta$	= property difference
$\varepsilon_{ij}$	= interaction energy parameter for contact of type $i-j$
$\Theta$	= unit surface fraction
$\Theta_{LK}$	= local unit surface fraction for units of type L around units of type K
$\theta$	= molecular surface fraction
$\theta_{ij}$	= local molecular surface fraction for molecule of type $i$ around molecule of type $j$
$\lambda$	= nonrandom auxiliary parameter
$\mu$	= chemical potential
$\mu_1^0$	= chemical potential of pure component 1
$v_{LM}$	= fraction of unit contacts of type L in a molecule of type M
$\phi_i$	= segment fraction of component $i$
$\chi_{ij}$	= Flory-Huggins interaction parameter
$\chi_{1,23}$	= quantity defined in ref 1

### Superscripts

*	= reducing quantities
$\sim$	= reduced quantities
0	= random values

### Subscripts

$i$	= quantity pertaining to component $i$
L	= quantity pertaining to unit L
LM	= quantity pertaining to unit L in component M

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