

# Estimation of polymer–polymer interaction density parameter by inverse gas chromatography

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The classical Flory–Huggins lattice model and Hildebrand–Scatchard solubility theory are used to develop a novel estimation scheme for determining the polymer–polymer interaction density parameter  $B_{23}$  from inverse gas chromatography data. The present considerations assume the binary interaction parameters to be concentration-dependent. It is shown that the parameter  $B_{23}$  is virtually independent of the nature of the probes. Finally, this procedure is performed on various blends of an ethylene–vinyl acetate copolymer and a chlorinated polyethylene with results substantiated by other experimental findings.

(Keywords: inverse gas chromatography; polymer–polymer interaction parameter; solubility parameter; copolymer/polymer blends; exothermic mixings)

## INTRODUCTION

Among other applications, inverse gas chromatography (i.g.c.) has been widely used<sup>1–4</sup> to determine the polymer–polymer interaction parameter, traditionally designated by  $\chi'_{23}$ . Basically, this technique monitors the retention volume  $V_g^0$  of a volatile probe (component 1), which is carried through the chromatography column, containing a molten polyblend of polymers 2 and 3, by the continuous flow of an inert gas. The classical thermodynamic considerations of the elution behaviour of this ternary system show that the polymer–polymer interactions are indeed intimately related to the physical characteristics of the probes<sup>2,4</sup>. As a result, the parameter  $\chi'_{23}$  derived from i.g.c. measurements is significantly dependent on the choice of the mobile phase, thus compromising the usefulness of the technique.

Hitherto, attempts have been made to rectify this adverse situation<sup>2–6</sup>. Deshpande *et al.* were the first to apply the recent equation-of-state theory in connection with i.g.c. studies of plasticized poly(dimethylsiloxane) using a variety of hydrocarbons as probes<sup>2</sup>. However, this model is rather sophisticated in that it requires a great deal of information, which is available only for a limited number of polymers<sup>7,8</sup>. In addition, it does not warrant predictions consistent with the experimental observations. Apparently, it is simpler to characterize the polymer–polymer interactions of a particular polyblend by the average value of  $\chi'_{23}$  collected from a series of probes<sup>3,6,9</sup>. Since pronounced discrepancy in  $\chi'_{23}$  is not uncommon, the uncertainty of this estimate may be substantial and unacceptable. The present work offers a practical solution to this problem.

## METHOD OF ESTIMATION

According to the classical Flory–Huggins theory of polymer solutions<sup>10</sup>, the free energy of mixing for the above ternary system,  $\Delta G_m$ , at temperature  $T$  is given by:

$$\Delta G_m = RT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + n_1 \phi_2 \chi_{12} + n_1 \phi_3 \chi_{13} + n_2 \phi_3 \chi_{23}) \quad (1)$$

where  $R$  is the gas constant, and  $n$ ,  $\phi$  and  $\chi$  are respectively the number of moles, normalized volume fraction and binary interaction parameter, with their subscripts 1, 2 and 3 designating the component numbers cited previously. Assuming the parameters  $\chi_{12}$ ,  $\chi_{13}$  and  $\chi_{23}$  to be concentration-dependent, one obtains at infinite dilution of the probe:

$$\left(\frac{\partial \Delta G_m}{\partial n_1}\right)_{P,T,n_2,n_3} = RT \left[ \ln \phi_1 + 1 - \frac{\bar{V}_1}{\bar{V}_2} \phi_2 - \frac{\bar{V}_1}{\bar{V}_3} \phi_3 + \phi_2 \chi_{12} + \phi_3 \chi_{13} - \frac{\bar{V}_1}{\bar{V}_2} \phi_2 \phi_3 \left(\frac{\partial \phi_3 \chi'_{23}}{\partial \phi_3}\right) \right] \quad (2)$$

where  $P$  is the pressure and  $\bar{V}$  denotes the molar volume. It follows that, under equilibrium conditions, usually attainable at a temperature approximately 50 K above the glass transition temperature, the overall polyblend–probe interaction parameter can be written as:

$$\chi_{1(23)} = \phi_2 \chi_{12} + \phi_3 \chi_{13} - \phi_2 \phi_3 \left(\frac{\partial \phi_3 \chi'_{23}}{\partial \phi_3}\right) \quad (3)$$

where

$$\chi'_{23} = (\bar{V}_1/\bar{V}_2) \chi_{23} \quad (4)$$

This parameter is readily determined by the standard i.g.c. procedure via:

$$\chi_{1(23)} = \ln \left( \frac{273.15R(w_2 v_2 + w_3 v_3)}{\bar{V}_1 P_1^0 V_g^0} \right) - \left( \frac{B_{11} - \bar{V}_1}{RT} \right) P_1^0 - \left[ 1 - \bar{V}_1 \left( \frac{\phi_2}{M_2 v_2} + \frac{\phi_3}{M_3 v_3} \right) \right] \quad (5)$$

where  $w$ ,  $v$  and  $M$  designate, respectively, the weight fraction, specific volume and molecular weight, and  $B_{11}$  and  $P_1^0$  are the second virial coefficient and saturated vapour pressure of the probe at  $T$  respectively. Equation (5) is valid for  $\phi_1 \approx 0$ . It may also be employed to compute  $\chi_{12}$  and  $\chi_{13}$  by setting  $w_3 = \phi_3 = 0$  and  $w_2 = \phi_2 = 0$  respectively. Clearly, the thermodynamic quantities  $\chi_{1(23)}$ ,

$\chi_{12}$  and  $\chi_{13}$  depend considerably on the physical properties of the low-molecular-weight solvents.

Recently, it has been shown that the polymer-probe interaction parameter obtained by i.g.c. measurements conforms remarkably well to Hildebrand-Scatchard solubility theory<sup>11-14</sup>. In this connection, we have:

$$\bar{\chi}_{jk} = \frac{(\delta_{0j} - \delta_{0k})^2}{RT} + \bar{\gamma}_{jk} \quad (6)$$

where  $\delta$  denotes the solubility parameter, and:

$$\bar{\chi}_{jk} = \chi_{jk}/\bar{V}_j \quad (7)$$

$$\bar{\gamma}_{jk} = \gamma_{jk}/\bar{V}_j \quad (8)$$

where  $\gamma_{jk}$  is the entropic component of  $\chi_{jk}$ . Here, the subscripts  $jk = 12, 13$  and  $23$ , whereas  $0j$  and  $0k$  attached to  $\delta$  identify the solubility parameters of the foregoing three components by assigning  $j$  or  $k$  equal to the component number.

Substituting equations (6)-(8) into (3) yields an expression for  $\chi_{1(23)}/\bar{V}_1$ , which resembles the former. In the Appendix, we show that these equations can be represented by a general expression:

$$\frac{\chi_{1(ij)}}{\bar{V}_1} = \bar{\chi}_{1(ij)} = \frac{(\delta_{01} - \delta_{ij})^2}{RT} + \bar{\gamma}_{1(ij)} \quad ij=02, 03, 23 \quad (9)$$

where

$$\delta_{ij} = \phi_i \delta_{0i} + \phi_j \delta_{0j} \quad (10)$$

$$\bar{\gamma}_{1(ij)} = \frac{\gamma_{1(ij)}}{\bar{V}_1} = \phi_i \bar{\gamma}_{1i} + \phi_j \bar{\gamma}_{1j} - \phi_i \phi_j \left( \frac{\partial \phi_j \bar{\gamma}_{ij}}{\partial \phi_j} \right) \quad (11)$$

with  $\phi_0 = 0$  and  $\phi_i + \phi_j = 1$  indicating  $\bar{\gamma}_{1(02)} = \bar{\gamma}_{12}$ ,  $\bar{\gamma}_{1(03)} = \bar{\gamma}_{13}$  and  $\bar{\chi}_{1(02)} = \bar{\chi}_{12}$ ,  $\bar{\chi}_{1(03)} = \bar{\chi}_{13}$ .

Equation (9) is converted to a useful form:

$$\frac{\delta_{01}^2}{RT} - \bar{\chi}_{1(ij)} = - \left( \frac{\delta_{ij}^2}{RT} + \bar{\gamma}_{1(ij)} \right) + \left( \frac{2\delta_{ij}}{RT} \right) \delta_{01} \quad (12)$$

If  $\bar{\gamma}_{1(ij)}$  is not a function of  $\delta_{01}$  (ref. 13), a plot of the left-hand side of equation (12) against  $\delta_{01}$  would produce a straight line with intercept and gradient providing the information on  $\bar{\gamma}_{1(ij)}$  and  $\delta_{ij}$  respectively. The solubility parameter of solvent  $\delta_{01}$  is computed by a method outlined by DiPaola-Baranyi *et al.*<sup>11</sup>. Equation (10) can be written in an alternative form:

$$\delta_{ij} = \delta_{02} + (\delta_{03} - \delta_{02})\phi_3 \quad (13)$$

where  $\delta_{ij} = \delta_{02}$ ,  $\delta_{03}$  or  $\delta_{23}$  depends on the value of  $\phi_3$ . Hence, a linear plot of  $\delta_{ij}$  against  $\phi_3$  furnishes the estimates of  $\delta_{02}$  and  $\delta_{03}$ . The derivative in equation (11) is accessible, once the parameter  $\bar{\gamma}_{1(23)}$ ,  $\bar{\gamma}_{12}$  and  $\bar{\gamma}_{13}$  have been established by equation (12). In the present analysis, we set:

$$f(\phi_3) = \partial \phi_3 \bar{\gamma}_{23} / \partial \phi_3 \quad (14)$$

which is treated as a polynomial empirically. Hence, we have from equations (6), (7) and (14):

$$\bar{\chi}_{23} = \frac{\chi_{23}}{\bar{V}_2} = \frac{(\delta_{02} - \delta_{03})^2}{RT} + \frac{1}{\phi_3} \int_0^{\phi_3} f(\phi_3) d\phi_3 \quad (15)$$

Equation (15) facilitates the calculation of the polymer-polymer interaction density parameter  $B_{23}$ , defined by:

$$B_{23} = RT \bar{\chi}_{23} \quad (16)$$

Unlike the parameter  $\chi'_{23}$ ,  $B_{23}$  is not related to  $\bar{V}_1$  explicitly.

## RESULTS AND DISCUSSION

Walsh and coworkers<sup>9</sup> have recently investigated the miscibility of an ethylene-vinyl acetate polymer (EVA 45) and a chlorinated polyethylene (CPE 3) by the i.g.c. method. Their experimental data are employed for the present purpose. The specific volumes of EVA 45 (component 2) and CPE 3 (component 3) are respectively estimated to be 1.229 and 0.817 ml g<sup>-1</sup> at 343.2 K and 1.262 and 0.847 ml g<sup>-1</sup> at 373.2 K. Other relevant information is detailed in ref. 9.

A typical plot constructed according to equation (12) is shown in Figure 1 for a total of five probes in a 75/25 blend of EVA 45/CPE 3 at 343.2 K. Other systems of interest have been analysed likewise. Table 1 lists the results on the thermodynamic parameters thus obtained for EVA 45, CPE 3 and their binary blends at 343.2 and 373.2 K.

In any event, the value of correlation coefficient  $r$  is close to unity, thus justifying the validity of equation (12). However, the foregoing linearity may result from the strong correlation between  $\delta_{01}^2$  and  $\delta_{01}$ . Hence, it is necessary to examine the consistency of the observed and predicted  $\bar{\chi}_{1(ij)}$  as shown in Table 2. The highest standard error of estimate,  $\sigma$ , defined in Table 2 is  $1.0 \times 10^{-3}$ , which corresponds to an error of  $\sim 10\%$  in  $\bar{\chi}_{1(ij)}$ . This value is indeed acceptable, considering the gross uncertainty in a number of parameters involved in equation (5), particularly  $V_g^0$ ,  $P_1^0$ ,  $M_2$  and  $M_3$  (ref. 4). Certainly, the accuracy of these measurable quantities can be greatly improved by a refined i.g.c. procedure recently proposed by El-Hibri *et al.*<sup>12,13</sup>. Although both polar and non-polar probes are utilized in this connection, they do not seem to display any specific interactions, which would invalidate the foregoing analysis based on the Hildebrand-Scatchard equation, with the polymers used. This is parallel to the work reported by others<sup>11,14-16</sup>, who have dealt with the polymer-probe systems exclusively. However, solvents of smaller size including acetone, methanol, chloroform and dichloromethane are found to deviate from equation (12) in the present study<sup>9</sup>.

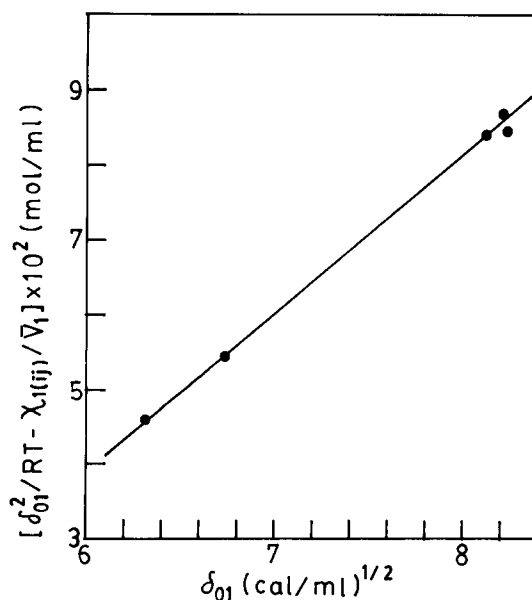


Figure 1 Linear plot of  $(\delta_{01}^2/RT - \bar{\chi}_{1(ij)}/\bar{V}_1)$  against  $\delta_{01}$  for the probes in a blend of EVA 45/CPE 3 with  $w_3 = 0.25$  at 343.2 K

**Table 1** Results obtained by equation (12) for polymeric systems containing EVA 45 and CPE 3

T (K)	Parameter	Composition of EVA 45/CPE 3, $w_3$				
		0.00	0.25	0.50	0.75	1.00
343.2	$\delta_{ij}$ (cal <sup>1/2</sup> ml <sup>-1/2</sup> )	7.01	7.15	7.33	7.76	8.59
	$\bar{\gamma}_{1(ij)} \times 10^2$ (mol ml <sup>-1</sup> )	1.0277	1.1677	1.2578	1.1191	1.1067
	$r^a$	0.9982	0.9986	0.9973	0.9995	0.9996
373.2	$\delta_{ij}$ (cal <sup>1/2</sup> ml <sup>-1/2</sup> )	6.26	6.74	6.84	7.37	7.80
	$\bar{\gamma}_{1(ij)} \times 10^2$ (mol ml <sup>-1</sup> )	1.2098	0.8421	1.2902	1.1528	1.3303
	$r^a$	0.9978	0.9981	0.9992	0.9991	0.9999

<sup>a</sup> Correlation coefficient

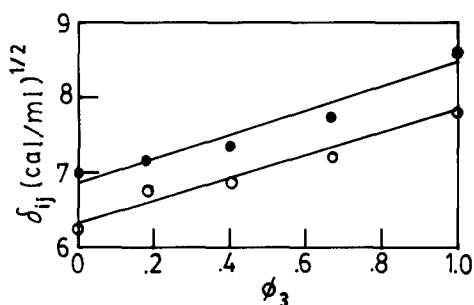
**Table 2** Comparison of observed and predicted  $\bar{\chi}_{1(ij)}$  for EVA 45/CPE 3 systems in various probes

T (K)	No.	Probe	$\delta_{01}$ (cal <sup>1/2</sup> ml <sup>-1/2</sup> )	$w_3=0$		$w_3=0.25$		$w_3=0.50$		$w_3=0.75$		$w_3=1.00$	
				$\bar{\chi}_{1(02)} \times 10^2$		$\bar{\chi}_{1(23)} \times 10^2$		$\bar{\chi}_{1(23)} \times 10^2$		$\bar{\chi}_{1(23)} \times 10^2$		$\bar{\chi}_{1(03)} \times 10^2$	
343.2	1	Ethyl acetate	8.13	1.17	1.21	1.30	1.31	1.35	1.35	1.23	1.14	1.22	1.14
	2	Tetrahydrofuran	8.22	1.09	1.24	1.19	1.33	1.23	1.37	1.07	1.15	—	—
	3	Diethyl ether	6.74	1.01	1.04	1.21	1.19	1.17	1.31	1.26	1.27	1.56	1.61
	4	n-Pentane	6.32	1.11	1.10	1.26	1.27	1.52	1.41	1.43	1.42	1.91	1.86
	5	2-Butanone	8.24	1.41	1.25	1.49	1.34	1.56	1.52	—	—	1.07	1.12
	6	$\sigma \times 10^{2c}$	—	0.10		0.09		0.10		0.06		0.06	
373.2	7	Ethyl acetate	7.89	1.38	1.57	0.92	1.02	1.41	1.44	1.10	1.19	1.29	1.33
	8	Tetrahydrofuran	8.07	1.72	1.65	1.02	1.08	1.47	1.49	1.22	1.22	1.38	1.34
	9	Diethyl ether	6.48	1.20	1.22	0.80	0.85	1.22	1.31	1.35	1.26	1.54	1.57
	10	n-Pentane	6.07	1.24	1.21	0.96	0.90	1.45	1.37	1.33	1.38	1.76	1.73
	11	2-Butanone	8.11	1.76	1.67	1.26	1.10	1.57	1.51	1.31	1.23	1.35	1.34
	12	$\sigma \times 10^{2c}$	—	0.10		0.095		0.06		0.07		0.03	

<sup>a</sup> Observed  $\bar{\chi}_{1(ij)}$

<sup>b</sup> Predicted  $\bar{\chi}_{1(ij)}$  by equation (9) based on the values of  $\delta_{ij}$  and  $\bar{\gamma}_{1(ij)}$  listed in Table 1

<sup>c</sup>  $\sigma = \left( \sum_j (\Delta_j^2/n) \right)^{1/2}$ , where  $\Delta_j$  is the difference between the observed and predicted  $\bar{\chi}_{1(ij)}$  for the  $j$ th probe, and  $n$  is the total number of probes studied


**Figure 2** Linear plots of  $\delta_{ij}$  against  $\phi_3$  for EVA 45/CPE 3 at 343.2 K (●) and 373.2 K (○)

The two sets of  $\delta_{ij}$  values included in Table 1 are plotted against  $\phi_3$  in Figure 2, which results in  $\delta_{02} = 6.87$  and  $\delta_{03} = 8.43$  cal<sup>1/2</sup> ml<sup>-1/2</sup> at 343.2 K, and  $\delta_{02} = 6.33$  and  $\delta_{03} = 7.82$  cal<sup>1/2</sup> ml<sup>-1/2</sup> at 373.2 K. Their respective  $r$  values are 0.9707 and 0.9879. Equation (11) leads to  $f(\phi_3)$ , which can be adequately expressed by the following quadratic functions:

$$f(\phi_3) \text{ (mol ml}^{-1}\text{)} = -0.00513 - 0.0273\phi_3 + 0.0486\phi_3^2 \quad (17)$$

$$f(\phi_3) \text{ (mol ml}^{-1}\text{)} = 0.0723 - 0.310\phi_3 + 0.316\phi_3^2 \quad (18)$$

for 343.2 and 373.2 K respectively. Consequently, equations (17) and (18), respectively, render:

$$B_{23} \text{ (cal ml}^{-1}\text{)} = -1.084 - 9.27\phi_3 + 11.05\phi_3^2 \quad (19)$$

$$B_{23} \text{ (cal ml}^{-1}\text{)} = 55.84 - 114.9\phi_3 + 77.9\phi_3^2 \quad (20)$$

which are independent of the nature of the probe, as expected.

In Figure 3, curves A and B are respectively derived from equations (19) and (20), and the data points are based on a method employed in the original paper<sup>9</sup>. The latter method rests on a dubious assumption that all binary interaction parameters are independent of the concentration of the polyblend. Basically, it computes the arithmetic mean of the  $\bar{\chi}_{23}$  values corresponding to the probes studied. It has been found that the standard error of  $y$  on  $\delta_{01}$ , where  $y$  denotes the left-hand side of equation (12), is consistently and significantly lower than the standard deviation from the mean of  $\bar{\chi}_{23}$ . This implies that the full curves in Figure 3 are more representative and reliable than the broken curves joining the data points. Indeed, our results demonstrate that mixtures of EVA 45 and CPE 3 in all proportions are exothermic at 343.2 K, due to specific interactions between the two polymers. This is positively confirmed by the phase diagram of the system, which exhibits a lower critical solution temperature significantly higher than 343.2 K<sup>17</sup>. Clearly, the intensity of the foregoing physical affinity is drastically reduced upon heating, as illustrated by curve B in Figure 3. In fact, the complementary study cited above has reported that phase separation in EVA 45/CPE 3 blends does occur for  $\phi_3 \geq 20\%$  at 373.2 K. In contrast, the predictions of the second approach seem to suggest that exothermic mixtures are effected at both tempera-

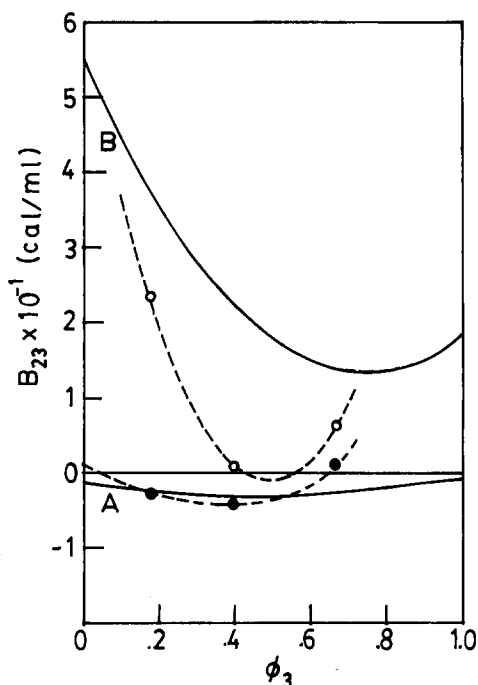


Figure 3 Composition dependences of  $B_{23}$  for EVA 45/CPE 3 at 343.2K (curve A) and 373.2K (curve B). The data points are obtained from the mean of  $\bar{\chi}_{23}$  for the four or five distinct probes designated by  $\bar{\chi}_{23}$ , via  $B_{23} = RT\bar{\chi}_{23}$ ; 343.2K (●) and 373.2K (○). The parameter  $\bar{\chi}_{23}$  is computed by  $\bar{\chi}_{23} = (\phi_2\bar{\chi}_{12} + \phi_3\bar{\chi}_{13} - \bar{\chi}_{1(23)})/\phi_2\phi_3$  as described in ref. 9

tures cited, but over certain ranges of  $\phi_3$  only, as inferred from the broken curves. Hence, the proposed algorithm is certainly more dependable in estimating the parameter  $B_{23}$ . The implication of the present finding is striking in that the conventional i.g.c. technique can now be applied effectively and routinely for the thermodynamic studies of the miscibility of polyblends.

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#### APPENDIX

According to equation (7), we have:

$$\chi_{12} = \bar{V}_1 \bar{\chi}_{12} \quad (\text{A.1})$$

$$\chi_{13} = \bar{V}_1 \bar{\chi}_{13} \quad (\text{A.2})$$

$$\chi_{23} = \bar{V}_2 \bar{\chi}_{23} \quad (\text{A.3})$$

Combining equations (4) and (A.3) yields:

$$\chi'_{23} = \bar{V}_1 \bar{\chi}_{23} \quad (\text{A.4})$$

Substituting equations (A.1), (A.2) and (A.4) into (3), we obtain:

$$\frac{\chi_{1(23)}}{\bar{V}_1} = \phi_2 \bar{\chi}_{12} + \phi_3 \bar{\chi}_{13} - \phi_2 \phi_3 \left( \frac{\partial \phi_3 \bar{\chi}_{23}}{\partial \phi_3} \right) \quad (\text{A.5})$$

Equation (6) results in:

$$\bar{\chi}_{12} = \frac{(\delta_{01} - \delta_{02})^2}{RT} + \bar{\gamma}_{12} \quad (\text{A.6})$$

$$\bar{\chi}_{13} = \frac{(\delta_{01} - \delta_{03})^2}{RT} + \bar{\gamma}_{13} \quad (\text{A.7})$$

$$\bar{\chi}_{23} = \frac{(\delta_{02} - \delta_{03})^2}{RT} + \bar{\gamma}_{23} \quad (\text{A.8})$$

Substituting equations (A.6)–(A.8) into (A.5), we obtain:

$$\frac{\chi_{1(23)}}{\bar{V}_1} = \frac{\phi_2(\delta_{01} - \delta_{02})^2 + \phi_3(\delta_{01} - \delta_{03})^2 - \phi_2\phi_3(\delta_{02} - \delta_{03})^2}{RT} + \bar{\gamma}_{1(23)} \quad (\text{A.9})$$

where

$$\bar{\gamma}_{1(23)} = \phi_2 \bar{\gamma}_{12} + \phi_3 \bar{\gamma}_{13} - \phi_2 \phi_3 \left( \frac{\partial \phi_3 \bar{\gamma}_{23}}{\partial \phi_3} \right) \quad (\text{A.10})$$

Equation (A.9) can be further simplified to:

$$\frac{\chi_{1(23)}}{\bar{V}_1} = \frac{(\delta_{01} - \delta_{23})^2}{RT} + \bar{\gamma}_{1(23)} \quad (\text{A.11})$$

where

$$\delta_{23} = \phi_2 \delta_{02} + \phi_3 \delta_{03} \quad (\text{A.12})$$

It can be shown that equations (A.6), (A.7) and (A.11) are readily generalized by equation (9), setting:

$$\bar{\chi}_{12} = \bar{\chi}_{1(02)} \quad (\text{A.13})$$

$$\bar{\chi}_{13} = \bar{\chi}_{1(03)} \quad (\text{A.14})$$

$$\bar{\gamma}_{12} = \bar{\gamma}_{1(02)} \quad (\text{A.15})$$

$$\bar{\gamma}_{13} = \bar{\gamma}_{1(03)} \quad (\text{A.16})$$