Polymers in Mixed Solvents: Feasibility of Computing Binary and Ternary Interaction Parameters from Intrinsic Viscosities Only

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Usually, intrinsic viscosities \( [\eta] \) of polymers in mixed solvents can be determined easily and reproducibly. As they depend on the thermodynamic interactions among components, it is attractive to estimate interaction parameters \( g \) directly from measurements of \( [\eta] \) as a function of solvent composition \( u_2 \) (for \( g \) and \( u_2 \), see eq 1). This has been attempted, for example, by Cowie and McCrindle\(^1\) and, more recently, by Dondos and Benoit.\(^2\) They determined binary interaction parameters between polymer and nonsolvent, but without accounting for the existence of a ternary interaction parameter.

The inclusion of such a parameter in the phenomenological expression for the Gibbs free energy of mixing has been advocated convincingly by Pouchly et al.\(^3\) They were the first to determine the ternary interaction function, together with binary polymer-nonsolvent interaction parameters, by combining the results of total sorption (Y) measurements (light scattering, osmometry, and viscometry) and preferential sorption (\( \lambda \)) measurements (dialysis experiments).\(^4\) Later, Chu and Munk\(^5\) and Aminabhavi and Munk\(^6\) developed methods to derive \( Y \) and \( \lambda \), and thus binary and ternary interaction functions, from measurements with the analytical ultracentrifuge. Horta et al.\(^7,8\) have given a statistical mechanical explanation for the ternary interaction function: it may be regarded as a modifier of binary parameters. Their explanation is based on an extension of the formalism outlined by Pouchly and Patterson.\(^9\)

The purpose of the calculations reported in this note is to investigate if an acceptable parameter \( g_{32} \) for the interaction between a polymer and a nonsolvent can be obtained together with the ternary interaction function from intrinsic viscosities only, even for the case of a "truncated" \([\eta]-u_2\) curve. Such curves may be restricted to the range \( 0.0 \leq u_2 \leq 0.5 \), for instance, because of demixing.

Determination of binary and ternary interactions in this experimentally simple way (as compared to other methods\(^9-12\)) would enable us to calculate and to understand tentatively a ternary (or rather pseudoternary)\(^10\) isothermal demixing diagram for a polymer-solvent-nonsolvent system,\(^11\) starting from the phenomenological expression of Pouchly et al.\(^3\) for the Gibbs free energy of mixing of such a system. In order to verify our method, we calculated \( g_{23} \) and \( g_T \) from the extensive viscosity data of Munk et al.,\(^12\) the interaction parameters of their systems being known independently, i.e., from combining the results of measurements\(^5,6\) of second virial coefficients \( A_2 \) and preferential adsorption parameters \( \lambda \).

Theory

We define the thermodynamic interaction parameters \( g_i \) and \( g_T \) by the Gibbs free energy of mixing \( \Delta G_m \) expressed as\(^5,6\)

\[
\Delta G_m / RT = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + g_{12} (u_{12}) n_1 \phi_2 + g_{13} (\phi_3) n_1 \phi_3 + g_{23} (\phi_2) n_2 \phi_3 + g_T (u_1, \phi_3) n_1 \phi_2 \phi_3 \tag{1}
\]

where indices 1 and 2 denote solvent components and index 3 denotes polymer. Numbers of moles are denoted by \( n_i \), volume fractions before mixing by \( \phi_i \), and solvent compositions by \( u_i \) or \( u_2 \).

\[
u_i = \phi_i / (\phi_1 + \phi_2)
\]

(2)

The notation \( g \) in this equation for the interaction parameters instead of the more usual\(^11-14\) notation \( \chi \) has been advocated by Koningsveld and Staverman,\(^10\) who related \( \chi \) to chemical potential rather than to Gibbs free energy. The \( g \) functions in (1) are functions not only of composition (as indicated) but also of molecular weight (distribution) and temperature.\(^10\)

The \( g \) functions may be related to intrinsic viscosities \([\eta]\), and in turn derived from them, only through a nonthermodynamic molecular model such as, for instance, the Flory-Fox model,\(^13\) which relates the molecular parameters molecular weight \( M_w \), unperturbed dimension \( K_f \), and linear expansion coefficient \( \alpha \) to the thermodynamic total sorption parameter \( Y \), a function of the interaction parameters \( g_{ij} \) and \( g_T \). In the derivation of the Flory-Fox model, \( Y \) has been supposed to be independent of molecular weight, though \( Y \) should depend on it (through \( g \)). We assume, then, that a phenomenological, molecular weight dependent \( Y \) may be derived from \([\eta]\), using equations like those of the Flory-Fox model:

\[
[\eta] = k_{\alpha} \alpha^{0.5} \tag{3}
\]

with

\[
\alpha = 2 C_M Y M_w^{0.5} \tag{3}
\]

where \( \alpha \) is the partial specific volume of the polymer and \( V_1 \) is the molar volume of component 1. (The constant \( C_M \) has been given in full elsewhere;\(^12,13\) it has been calculated with 0.365 assuming a value of 2.5 \times 10^{29} \text{(cgsu)} for Flory's universal viscosity constant \( \Phi_u \).)

A thermodynamically exact expression for \( Y \) in the limit \( \phi_2 \to 0 \) has been derived from (1) by Pouchly et al. It reads in the \( g \) notation of Chu and Munk\(^5\)

\[
Y = \sqrt{b_{23} - b_{23} b_{23}^3} / b_{23} \tag{4}
\]

with

\[
b_{23} = u_{12} + u_{23} + u_{23} \left[ 2 \left( g_{12} (u_{12}) - g_{12} (u_{12}) - 1 \right) \right]^{-1}
\]

(5)

\[
Y = x_3^o + x_3^o (u_3^0 - 2 u_3^o u_3 (x_3^o) - 2 x_T^o u_3 u_2)
\]

where \( x_3^o \) is the modified second virial coefficient \( A_2 \) and preferential adsorption parameter \( \lambda \).

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For the exemplary systems of our calculations it turned out that we could derive $Y$ values through (3) that were within experimental error and in accordance with $Y$ values determined in a thermodynamically exact way (from second virial coefficients). Thermodynamical equations less exact than (4) are the Shultz–Flory equation[14] (cf. also ref 1, 2, and 12) and the so-called one-liquid approximation. The former is obtained by putting $x_{13} = x_{13}^o = g_{13}$ (i.e., by neglecting the initial $v_3$ dependence) and $x_{13}^o = g_{13}^o = 0$ (i.e., by ignoring the ternary interaction functions). It gives a poor representation of a measured $[\eta] - u_2$ curve in terms of $x_{13}^o$. The one-liquid approximation is obtained essentially by putting $Y = 1/2g_{23}$, i.e., by assuming that the preferential sorption $\lambda$ (proportional to $b_{23}/b_{23}^o$) is zero. This may be useful as an approximation in the vicinity of a maximum in the $Y - u_2$ curve.

Outline of Procedure

If a number, say $M$, of $[\eta]$ values has been determined, we can now calculate $M$ values of $Y$ through (3) or another adequate model. Thus, we have obtained $M$ nonlinear equations (4) in $\leq M$ unknowns, the unknowns being coefficients of functions of $u_1$ and/or $\phi_3$ that describe the $g_{13}$ and $g_{12}$. In order to solve such a set of nonlinear equations satisfactorily (the $Y$ being data of limited accuracy), there should be few unknowns compared to the number of equations, $M$.

When our goal is restricted to the determination of the polymer–nonsolvent interaction parameter $x_{13}^o$ and the ternary parameters $x_{13}^o$ and $g_{13}^o$, we have to insert in the $M$ $Y$ equations as accurate values as possible for the coefficients of $g_{13}$ as a function of $u_2$. It has been pointed out by several authors that this function determines the $Y - u_2$ curve to a large extent. The accuracy of the calculated $x_{13}^o$ and $g_{13}^o$ may be improved further, as mentioned, by reducing the number of unknowns. Thus, we can assume $x_{13}^o$ and $g_{13}^o$ to be constants (independent of $u_2$ or $x_T^o$) to be a constant and equal to $g_{13}^o$. (The latter assumption deprives us of desirable information about the initial dependence of $g_{13}$ on $\phi_3$, however.)

A further reduction of the number of unknowns is to assume $g_{13}^o = g_{13}^o$ to be zero. This is justifiable when solvent and nonsolvent do not differ too much in solvent quality. Numerical calculation of values for this parameter from the $M$ nonlinear equations may even lead to nonsensical results when it is very small.

Calculations

From $Y$ values obtained from the $[\eta]$ determined by Aminabhavi and Munk[8] and eq 3, we calculated $x_{13}^o$ (or $g_{13}^o = g_{13}^o$, with $x_{13}^o$ as known) and $x_{13}^o$ and $g_{13}^o$, for which we assumed cubic expansions in $u_2$:

$$g_{13}^o = (g_{13}^o)_{0} + (g_{13}^o)_{1}u_2 + (g_{13}^o)_{2}u_2^2 + (g_{13}^o)_{3}u_2^3 \quad (5)$$

$$x_{13}^o = (x_{13}^o)_{0} + (x_{13}^o)_{1}u_2 + (x_{13}^o)_{2}u_2^2 + (x_{13}^o)_{3}u_2^3 \quad (6)$$

(For the desirable number of $g_{13}^o$ or $x_{13}^o$ parameters see the Results and Discussion sections.) Thus, our maximum number of unknowns was nine: one for $x_{13}^o$ or $g_{13}^o = g_{13}^o$ and eight for $x_{13}^o$ and $g_{13}^o$. We calculated these parameters by applying a computer program for the solution of a set of $N$ nonlinear equations in $N$ unknowns (with $N \leq M$). We used program EMOPDF of the Numerical Algorithms Group.15

Input values for $Y$ were calculated through (3) directly from the $[\eta]$ of Tables I and II of ref 12, with $K_w = 8.55 \times 10^{-2}$ for polystyrene in benzene/cyclohexane mixtures and $K_w$ for polystyrene in ethyl acetate/cyclohexane mix-

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Table I

<table>
<thead>
<tr>
<th>Functions $g_{13}^o$ and $x_{13}^o$ (Full Eq 5 and 6) and $g_{13}^o = g_{13}^o$, Calculated from Nine Values for $Y$ Derived from Literature $[17]$</th>
<th>$u_2$</th>
<th>$g_{13}^o$</th>
<th>$x_{13}^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.008</td>
<td>0.00</td>
<td>0.12</td>
</tr>
<tr>
<td>0.2</td>
<td>0.017</td>
<td>0.017</td>
<td>0.12</td>
</tr>
<tr>
<td>0.4</td>
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<td>0.022</td>
<td>0.12</td>
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<tr>
<td>0.6</td>
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<td>0.024</td>
<td>0.12</td>
</tr>
<tr>
<td>0.8</td>
<td>0.015</td>
<td>0.015</td>
<td>0.12</td>
</tr>
<tr>
<td>1.0</td>
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<td>0.18</td>
<td>-0.20</td>
</tr>
</tbody>
</table>

Table II

<table>
<thead>
<tr>
<th>Binary Parameter $x_{13}^o$ and Ternary Parameters $(g_{13}^o)$, and $(x_{13}^o)$, (See Eqs 5 and 6) Calculated from Five Values for $Y$ (Cf. Table I)</th>
<th>$u_2$</th>
<th>$(g_{13}^o)$</th>
<th>$(x_{13}^o)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
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<tr>
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<td>0.4</td>
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<td>0.022</td>
</tr>
<tr>
<td>0.6</td>
<td>0.024</td>
<td>0.024</td>
<td>0.024</td>
</tr>
<tr>
<td>0.8</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
</tr>
<tr>
<td>1.0</td>
<td>-0.035</td>
<td>0.07</td>
<td>-0.035</td>
</tr>
</tbody>
</table>

$^\alpha$ System: ethyl acetate (1)-cyclohexane (2)-poly-styrene (3). Input constants: $f_{13} = 0.0039$, $x_{13}^o = 0.492$, $x_{13}^o = 0.222$, $X_T^o$, from ref 6. Calculated: $y_{13}^o = g_{13}^o = -0.07$ (lit.: $-0.0003$).

Notes

For brevity, we present only results of calculations for the system polystyrene/ethyl acetate/cyclohexane. All other results show the same trends. In order to give an idea of the accuracy of our method, we present calculations of $y_{13}^o = g_{13}^o$, $g_{13}^o$, and $x_{13}^o$ first and compare them (Table I) to those obtained by Chu and Munk[8] through a fully different calculation procedure involving preferential adsorption data $\lambda$ primarily and $Y$ data in addition.

As Table I shows, the $Y - u_2$ curve is described satisfactorily, but $y_{13}^o = g_{13}^o$ and the functions $g_{13}^o$ and $x_{13}^o$ do not reproduce the values of Munk et al[5,6]. This may be attributed to our assumptions about $x_{13}^o$ and $g_{13}^o$ (cubic polynomials may be inadequate representations for their actual course with $u_1$) and/or to our calculation procedure:
nine variables (one of them, $\log_{23}^o - \log_{13}^o$, very small\cite{56}) may be too many with respect to the nine equations $Y$.

When we put $x_{10}^o = (x_{1T}^o)_0$ and $g_{1T}^o = (g_{1T}^o)_0$ with $lg_{23}^o - lg_{13}^o = 0.0$, we found reasonable $x_{23}^o$ values, and reasonable "averaged" values for $g_{5}^o$ and $x_{1T}^o$, even from a "truncated" $Y$-$u_2$ curve (Table II). The $Y$-$u_2$ curve in this case is described as well as it is in Table I. We ascribe this to the fact that the $Y$-$u_2$ curve is determined to a large extent by the $g_{12}$ function\cite{45} (which is the same in Tables I and II).

Inclusion of the $\lambda$ values of Chu and Munk\cite{6} in our calculations did not give results better than those represented in Table I or II. They became even worse as regards $x_{23}^o$ and $g_{5}^o$. Fully nonsensical results for $g_{5}^o$ and $x_{1T}^o$, as well as a bad reproduction of the $Y$-$u_2$ curve, were obtained with $\lambda = 0$. Thus the single-liquid approximation appears to be inappropriate for our procedure.

Discussion

Handling a restricted range of $Y$ data as a system of $M$ nonlinear equations in $N$ unknowns may give a reasonable estimation of $x_{23}^o$ and of $g_{5}^o$ and $x_{1T}^o$ (and thus of the initial slope of $g_{1T}^o$ to $g_{2}^o$). This might be sufficient for instance, for a tentative calculation of a ternary isothermal demixing diagram for a polymer-solvent-non solvent system.

The approximate calculation of $g$ parameters as proposed in this paper only works when several requirements are fulfilled. First, $g_{12}$ has to be known over the whole solvent composition range. Second, the solvents should not differ too much in quality: the assumption that $lg_{23}^o$ be too many with respect to the nine equations $Y$.

A final objection that might be raised against our procedure has to do with the physical meaning of $g_{5}^o$ and thus with our eq 1, i.e., with the extension by Pouchlé et al. of the Flory–Huggins expression for the free energy of mixing.\cite{34} Horta and Fernández-Piérola argue that derivatives like $\partial g_{5}^o/\partial u_i$ and $(\partial g_{5}^o/\partial \phi_{3})$,

$\partial Y$ (eq 4) and in the preferential sorption parameter\cite{9-16} $\lambda$, are empirical parameters lacking a clear physical meaning. Furthermore, according to these authors, including such derivatives in calculations (i.e., putting $g_{5}^o \neq x_{1T}^o$) does not improve the simultaneous representation of $Y$ and $\lambda$ as functions of $u_2$ (this, however, is not in accordance with Chu and Munk’s findings\cite{9-16}). Horta and Fernández-Piérola therefore prefer the use of one adjustable parameter, a physical meaning based on the Flory–Pricigine–Patterson theory:

$\text{References and Notes}$

(7) Horta, A. Macromolecules 1979, 12, 785.
(9) Pouchlé, J.; Patterson, D. Macromolecules 1976, 9, 574.
(13) Flory, P. J.; Fox, T. G. J. Am. Chem. Soc. 1951, 73, 1904.

Athermal Exchange between Lithium Salts of High Molecular Weight Living Polymers and the Analogous Salts of Oligomers in Hydrocarbon Solvents

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In a paper published in Macromolecules,\textsuperscript{1} Morton, Pett, and Fetters presented a proof of the dimeric nature of lithium salts of living polymers in hydrocarbon solvents based on the athermal exchange between the aggregates of high molecular weight salts, (PM-Li\textsuperscript{+}), and analogous oligomeric salts, (RM-Li\textsuperscript{+}),. The aggregates are in a rapidly established dynamic equilibrium with minute fractions of lower aggregates; e.g., dimeric aggregates are in equilibrium with their monomeric polymers

\[(\text{PM-Li}^+) + (\text{RM-Li}^+) \rightleftharpoons 2\text{PM-Li}^+
\]

\[(\text{RM-Li}^+) + (\text{PM-Li}^+) \rightleftharpoons 2\text{RM-Li}^+
\]

The above reactions represent homodimerizations; i.e., the dimers are formed by the association of any two monomeric species. Since the end groups responsible for the association are similar for the high molecular salt and the oligomeric salt, one expects $K_d$, provided that the degree of polymerization of the oligomers is not too low, say 10. This indeed was assumed by the authors.

The rapid dissociation–association leads to the formation of heterodimers when $(\text{PM-Li}^+) + (\text{RM-Li}^+)$ are mixed together

\[(\text{PM-Li}^+) + (\text{RM-Li}^+) \rightleftharpoons 2\text{PM-Li}^+; 2\text{RM-Li}^+
\]

and their proportion in equilibrated mixtures could be determined by a viscometric technique. For concentrated solutions of high molecular weight polymers in the entanglement region, their viscosity, $\eta$, is proportional to power $\alpha$ of the weight-average molecular weight of the dissolved polymers; viz, $\eta \propto M^\alpha$, with $\alpha$ being in the range 3.3-3.5. Hence, the viscosity of a solution of uniform, high molecular weight dimers decreases by a factor of $2^\alpha \approx 10$.