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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 Pouchlý et al.[3,4] 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 (λ) measurements (dialysis equilibrium).[3,4] Later, Chu and Munk[5] and Aminabhavi and Munk[6] developed methods to derive Y and λ, 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 Pouchlý and Patterson.[9]

The purpose of the calculations reported in this note is to investigate if an acceptable parameter g_{23} 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[3-6]) 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 Pouchlý et al.[3,4] 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 λ.

Theory

We define the thermodynamic interaction parameters g_{ij} and g_T by the Gibbs free energy of mixing ΔG_m expressed as[3-5]

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

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 ϕ_i, and solvent compositions by u_1 or u_2:

$$u_1 \equiv \phi_1/(\phi_1 + \phi_2)$$

$$u_2 \equiv \phi_2/(\phi_1 + \phi_2) \quad (2)$$

The notation g in this equation for the interaction parameters instead of the more usual[1-4,12] notation χ has been advocated by Koningsveld and Staverman,[10] who related χ 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 $\bar{M}_w$, unperturbed dimension K_θ, and linear expansion coefficient α 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:

$$[\eta] = K_\theta \alpha^3 \bar{M}_w^{0.5}$$

$$\alpha^5 - \alpha^3 = 2C_M Y \bar{M}_w^{0.5} \quad (3)$$

with

$$C_M = 0.356(\bar{v}_3^2/V_1)K_\theta^{-1}$$

where $\bar{v}_3$ 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 0.356 assuming a value of 2.5×10^{23} (cgsu) for Flory's universal viscosity constant Φ_0.)

A thermodynamically exact expression for Y in the limit $\phi_3 \rightarrow 0$ has been derived from (1) by Pouchlý et al. It reads in the g notation of Chu and Munk[5]

$$Y = \tfrac{1}{2}(b_{33} - u_1u_2b_{23}^2/b_{22}) \quad (4)$$

with

$$b_{22} = u_1 l + u_2 - u_1u_2\left\{2\left[g_{12} + (u_1 - u_2)\frac{\partial g_{12}}{\partial u_1}\right] - u_1u_2\frac{\partial^2 g_{12}}{\partial u_1^2}\right\}$$

$$b_{23} = (lg_{23}^\circ - g_{13}^\circ) + 1 - l - (u_1 - u_2)(g_{12} - g_T^\circ) + u_1u_2\left(\frac{\partial g_{12}}{\partial u_1} - \frac{\partial g_T^\circ}{\partial u_1}\right)$$

$$b_{33} = u_1 + u_2 l + 2u_1u_2(g_{12} - g_T^\circ) - 2(u_1\chi_{13}^\circ + u_2 l\chi_{23}^\circ) - 2\chi_T^\circ u_1u_2$$

$$l = V_1/V_2 \text{ (molar volume ratio)}$$

$$\chi_{i3}^\circ = g_{i3} - (\partial g_{i3}/\partial \phi_3)^\circ$$

$$\chi_T^\circ = g_T^\circ - (\partial g_T/\partial \phi_3)_{u_1}^\circ$$

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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[5]).

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 $\chi_{i3} \equiv \chi_{i3}^\circ = g_{i3}$ (i.e., by neglecting the initial ϕ_3 dependence) and $\chi_T^\circ = g_T^\circ = 0$ (i.e., by ignoring the ternary interaction functions). It gives a poor representation of a measured $[\eta]$–u_2 curve in terms of χ_{i3}.[12] The one-liquid approximation is obtained essentially by putting $Y = {}^1/_2 b_{33}$, i.e., by assuming that the preferential sorption λ (proportional to b_{23}/b_{22}) is zero. This may be useful as an approximation in the vicinity of a maximum in the Y–u_2 curve.[8]

Outline of Procedure

If a number, say M, of $[\eta]$ values has been determined, we now can 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 ϕ_3 that describe the g_{ij} and g_T. 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 χ_{23}° and the ternary parameters χ_T° and g_T°, we have to insert in the M Y equations as accurate values as possible for the coefficients of g_{12} 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.[4,6,8] The accuracy of the calculated χ_{23}°, χ_T°, and g_T° may be improved further, as mentioned, by reducing the number of unknowns. Thus, we can assume χ_T° and g_T° to be constants (independent of u_2) or χ_T° to be a constant and equal to g_T°. (The latter assumption deprives us of desirable information about the initial dependence of g_T on ϕ_3, however.)

A further reduction of the number of unknowns is to assume $lg_{23}^\circ - g_{13}^\circ$ 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[6] and eq 3, we calculated χ_{23}° (or $lg_{23}^\circ - g_{13}^\circ$, with χ_{23}° as known) and χ_T° and g_T°, for which we assumed cubic expansions in u_2:

$$g_T^\circ = (g_T^\circ)_0 + (g_T^\circ)_1 u_2 + (g_T^\circ)_2 u_2^2 + (g_T^\circ)_3 u_2^3 \quad (5)$$

$$\chi_T^\circ = (\chi_T^\circ)_0 + (\chi_T^\circ)_1 u_2 + (\chi_T^\circ)_2 u_2^2 + (\chi_T^\circ)_3 u_2^3 \quad (6)$$

(For the desirable number of g_T° or χ_T° parameters see the Results and Discussion sections.) Thus, our maximum number of unknowns was nine: one for χ_{23}° or $lg_{23}^\circ - g_{13}^\circ$ and eight for χ_T° and g_T°. We calculated these parameters by applying a computer program for the solution of a set of M nonlinear equations in N unknowns (with $N \leq M$). We used program E04FDF 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 $K_\theta = 8.55 \times 10^{-2}$ for polystyrene in benzene/cyclohexane mixtures and K_θ for polystyrene in ethyl acetate/cyclohexane mixtures as given by Table IV of ref 12. V_1 and V_2 were also from ref 12, and the $\bar{v}_3$ were from ref 6. The Y thus calculated agreed within ±0.003 or better with the Y calculated from the A_2 of ref 5 through $Y = A_2 V_1/\bar{v}_3^2$. Thus for the systems studied by Munk and co-workers, the Flory–Fox model for the description of the dependence of $[\eta]$ on solvent composition is appropriate.

Table I

Functions g_T° and χ_T° (Full Eq 5 and 6) and $eg_{23}^\circ - g_{13}^\circ$ Calculated from Nine Values for Y Derived from Literature $[\eta]$–u_2 Data[12] through Eq 3 and 4[a]

	Y		g_T°		χ_T°	
u_2	exptl	calcd	calcd	ref 6	calcd	ref 6
0.0	0.008	0.008	0.00	0.80	0.12	0.30
0.2	0.017	0.017	0.05	0.75	0.67	0.30
0.4	0.022	0.022	0.09	0.70	0.88	0.35
0.6	0.024	0.024	0.15	0.60	0.78	0.45
0.8	0.015	0.015	0.16	0.55	0.48	0.35
1.0		−0.020	0.18	0.40	−0.20	0.10

[a] System: ethyl acetate (1)–cyclohexane (2)–polystyrene (3). Input constants:[5,12] $l = 0.9039$, $\chi_{13}^\circ = 0.492$, $\chi_{23}^\circ = 0.522$, g_{12} from ref 6. Calculated: $lg_{23}^\circ - g_{13}^\circ = -0.07$ (lit.:[6] −0.0003).

Table II

Binary Parameter χ_{23}° and Ternary Parameters $(g_T^\circ)_0$ and $(\chi_T^\circ)_0$ (See Eq 5 and 6) Calculated from Five Values for Y (Cf. Table I)[a]

	Y		$(g_T^\circ)_0$		$(\chi_T^\circ)_0$	
u_2	exptl	calcd	calcd	ref 6	calcd	ref 6
0.0	0.008	0.008	0.70	0.80	0.33	0.30
0.2	0.017	0.016	0.70	0.75	0.33	0.30
0.4	0.022	0.021	0.70	0.70	0.33	0.35
0.6	(0.024)	0.018	0.70	0.60	0.33	0.45
0.8	(0.015)	−0.005	0.70	0.55	0.33	0.35
1.0		−0.035	0.70	0.40	0.33	0.10

[a] Experimental values in parentheses were not input in the computer program. Input constants as in Table I, with $lg_{23}^\circ - g_{13}^\circ = 0.0$ instead of χ_{23}°. Calculated: $\chi_{23}^\circ = 0.502$ (lit.:[6] 0.522–0.534).

For g_{12} we applied quadratic expressions in u_2 throughout, the numerical values of the coefficients being given in ref 6.

When calculating $lg_{23}^\circ - g_{13}^\circ$ as a variable, we put the χ_{23}° as the ones given by Chu and Munk.[5] As they found that $lg_{23}^\circ - g_{13}^\circ$ was rather small ($<|0.06|$) for both systems they studied, we felt justified in assuming $lg_{23}^\circ - g_{13}^\circ = 0.0$ when calculating χ_{23}° as a variable. A Y value at $u_2 = 0.0$ was not considered as one of the M nonlinear equations to be solved, giving χ_{13}° directly through $Y = {}^1/_2 - \chi_{13}^\circ$.

Results

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 $lg_{23}^\circ - g_{13}^\circ$, g_T°, and χ_T° first and compare them (Table I) to those obtained by Chu and Munk[5,6] through a fully different calculation procedure involving preferential adsorption data λ primarily and Y data in addition.

As Table I shows, the Y–u_2 curve is described satisfactorily, but $lg_{23}^\circ - g_{13}^\circ$ and the functions g_T° and χ_T° do not reproduce the values of Munk et al.[5,6] This may be attributed to our assumptions about χ_T° and g_T° (cubic polynomials may be inadequate representations for their actual course with u_1) and/or to our calculation procedure:

nine variables (one of them, $lg_{23}^\circ - g_{13}^\circ$, very small[5,6]) may be too many with respect to the nine equations Y.

When we put $\chi_T^\circ \equiv (\chi_T^\circ)_0$ and $g_T^\circ \equiv (g_T^\circ)_0$ with $lg_{23}^\circ - g_{13}^\circ = 0.0$, we found reasonable χ_{23}° values, and reasonable "averaged" values for g_T° and χ_T°, 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[4,6,8] (which is the same in Tables I and II).

Inclusion of the λ values of Chu and Munk[5,6] in our calculations did not give results better than those represented in Table I or II. They became even worse as regards χ_T° and g_T°. Fully nonsensical results for g_T° and χ_T°, 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 χ_{23}° and of g_T° and χ_T° (and thus of the initial slope of g_T° to ϕ_3). This might be sufficient for instance, for a tentative calculation of a ternary isothermal demixing diagram for a polymer–solvent–nonsolvent system.[11]

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 $lg_{23}^\circ - g_{13}^\circ$ is negligibly small turned out to be rather crucial to our results for χ_{23}°, χ_T°, and g_T°. Third, the theory for the calculation of Y from $[\eta]$ should be adequate for the system in question and allow the calculation of thermodynamically right (and molecular weight dependent) Y values. Fourth, K_θ has to be known, and finally, Φ_0 has to be established separately for the studied system when the "universal" value of 2.5×10^{23} appears to be incompatible[16] with K_θ determined in several independent ways.

Thus we were not able to extract a consistent set of K_θ and Φ_0 values from the literature[16] for the system cellulose acetate–acetone–water. We therefore did not succeed in calculating g parameters for this system from $[\eta]$ data in accordance with g parameters determined from λ and A_2, as published elsewhere.[11]

An objection to our application of the NAG procedure E04FDF might be that the results depend slightly on initial guesses of parameters, even when the output of E04FDF is such as to indicate that the parameters calculated are real minima at the data set introduced. A more elaborate numerical procedure might give better results. We did not pursue this matter further.

A final objection that might be raised against our procedure has to do with the physical meaning of g_T° and thus with our eq 1, i.e., with the extension by Pouchlý et al. of the Flory–Huggins expression for the free energy of mixing.[3,4] Horta and Fernándex–Piérola argue that derivatives like $\partial g_T^\circ / \partial u_1$ and $(\partial g_T / \partial \phi_3)^\circ$, figuring in Y (eq 4) and in the preferential sorption parameter[3–6] λ, are empirical parameters lacking a clear physical meaning. Furthermore, according to these authors, including such derivatives in calculations (i.e., putting $g_T^\circ \neq \chi_T^\circ$) does not improve the simultaneous representation of Y and λ as functions of u_2 (this, however, is not in accordance with Chu and Munk's findings[5,6]). Horta and Fernándex–Piérola therefore prefer the use of one adjustable parameter, with a physical meaning based on the Flory–Prigogine–Patterson theory:[9] the contact surface of the polymer molecule. Such a parameter, however, could be calculated easily with our procedure in the same way as we calculated g_T° and χ_T°.

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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*,[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, $(P_nM^-,Li^+)_n$, and analogous oligomeric salts, $(RM^-,Li^+)_n$. 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

$$(PM^-,Li^+)_2 \overset{K_1}{\rightleftharpoons} 2PM^-,Li^+$$

$$(RM^-,Li^+)_2 \overset{K_2}{\rightleftharpoons} 2RM^-,Li^+$$

The above reactions represent *homo*dimerizations; 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 $K_1 = K_2$, 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 *hetero*dimers when $(PM^-,Li^+)_2$ and $(RM^-,Li^+)_2$ are mixed together

$$(PM^-,Li^+)_2 + (RM^-,Li^+)_2 \overset{K_{ex}}{\rightleftharpoons} 2(PM^-,Li^+;RM^-,Li^+)$$

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, η, is proportional to power α of the weight-average molecular weight of the dissolved polymers; viz, $\eta \sim \bar{M}_w^{\alpha}$, with α 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 $2^\alpha \approx 10$

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