Flory-Rehner free energy of mixing[1] and fitting the data to a Flory-Huggins parameter $\chi = \chi_2 + \chi_3\phi$. When this is done, a difference in $\chi$ subsists between the present samples and the more homogeneous gels of ref 7, which indicates a short fall in swelling pressure (i.e., an apparent excess elastic energy) at $\phi \simeq 1$ of the same sign and order of magnitude as found for other systems in ref 2 and 3. The conclusions of this note remain unchanged in this analysis.

**Registry No.** (Acrylamide)(methylenebisacrylamide) (copolymer), 25034-58-6.

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# Prediction of Ternary Effects in Polymer-Mixed Solvent Systems

ARTURO HORTA

*Departamento de Química Física, Facultad de Ciencias, Universidad a Distancia (UNED), 28040 Madrid, Spain.*

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Polymers in mixed solvents present new interesting phenomena; among them, cosolvency and preferential adsorption are notable examples. Properties measuring coil dimensions and excluded volume, such as intrinsic viscosity, $[\eta]$, second virial coefficient, $A_2$, or the interaction parameter from a Stockmayer-Fixman plot, $B$, are solvent composition dependent in a mixed solvent. The simplest behavior to be imagined is that the value of the property in a mixed solvent be intermediate between the values in the two pure liquids. However, the behavior observed is more complex. Large deviations from the linear interpolation between the two pure liquid values are often found.[1-6] Differences between measured and interpolated $[\eta]$ as large as 200% have been reported in cosolvent systems.[6]

The preferential adsorption coefficient, $\lambda$, can also present peculiar variations with solvent composition. The simplest behavior to be imagined for $\lambda$ is that the solvent preferentially adsorbed always be the better solvent of the polymer. But the real situation is also more complex. There are numerous examples in which the poor solvent is preferentially adsorbed.[7] Even strong precipitants of the polymer can adsorb preferentially to it.[4,8] Often, one of the two liquids in the mixed solvent is preferentially adsorbed in a certain range of solvent compositions, while the other liquid is preferentially adsorbed in the rest of the composition range, giving thus an inversion in $\lambda$.[1,4,6,8-10]

For the theoretical description of excluded volume properties ($[\eta]$, $A_2$, $B$) and of preferential adsorption ($\lambda$), thermodynamic theory has been applied, first, the Flory-Huggins model (FH)[11,12] and, later, equation of state theory (Flory, Prigogine, Patterson formalism, FPP).[13-15] In the FH formalism, the noncombinatorial part of $\Delta G_M$ (Gibbs mixing function) for a ternary 1,2,3 system is written as a sum of binary terms (1-2, 1-3, 2-3), each one depending on a binary interaction parameter, $g_{ij}$. The form of these binary terms is $n_i\phi_j g_{ij}$ ($n$ = amount of substance; $\phi$ = volume fraction).

This FH formalism was found to cause difficulties in interpreting the properties of ternary systems composed of a polymer and a mixed solvent. Its applicability was then extended by introducing a ternary interaction parameter, $g_T$, contributing a term $n_1\phi_2\phi_3 g_T$ to $\Delta G_M$.[16,17] This extra ternary term is a correction that destroys the additivity of binaries in $\Delta G_M$ and has been considered as taking into account "ternary effects".

The principles underlying the FPP formalism are different. In no moment is $\Delta G_M$ assumed to be a sum of binary terms. All terms depend simultaneously on the properties of the ternary system, because the variable on which $\Delta G_M$ depends is the reduced temperature of the system, $\tilde{T}$, defined as[15]

$$\tilde{T} = (n_1p_1{}^*V_1{}^*\tilde{T}_1 + n_2p_2{}^*V_2{}^*\tilde{T}_2 + n_3p_3{}^*V_3{}^*\tilde{T}_3)/ \\ (n_1p_1{}^*V_1{}^*\tilde{T}_1 + n_2p_2{}^*V_2{}^*\tilde{T}_2 + n_3p_3{}^*V_3{}^*\tilde{T}_3 - \\ n_1\theta_2V_1{}^*X_{12} - n_1\theta_3V_1{}^*X_{13} - n_2\theta_3V_2{}^*X_2) \quad (1)$$

($p_i{}^*$, $V_i{}^*$, $T_i{}^*$ = reduction parameters for pressure, molar volume, and temperatures; $\tilde{T}_i = T/T_i{}^*$; $\theta_i$ = molecular surface fraction; $X_{ij}$ = exchange interaction energy density). The composition and characteristic parameters of the three components, as well as the exchange interaction energy densities for all three pair interactions ($X_{12}$, $X_{13}$, $X_{23}$), contribute simultaneously in defining $\tilde{T}$ of the ternary system.

Thus, one of the advantages of FPP formalism over FH for ternary systems is that it obviates any assumption about the additivity of binary terms. This advantage can be of use not only for polymer-mixed solvent systems but *also for two polymers in one solvent systems.*

Since FPP results are intrinsically ternary, it is possible to obtain with them a theoretical derivation of the error, which is committed when additivity of binaries is assumed. In other words, with the FPP formalism it is possible to estimate the ternary correction ($g_T$) needed in the FH results. This evaluation of the ternary correction for $\lambda$ and for $Y$ has already been given in detail.[15] ($Y$ = total sorption potential, obtained from $[\eta]$, from $A_2$, or from $B$).

The FPP theory takes into account the dissimilarity in contact surface and in free volume between polymers and liquids, which the FH theory neglects. Since these dissimilarities have an important effect on $\lambda$ and $Y$, it is reasonable to think that the ternary correction ($g_T$) needed in FH is in part due to these neglected dissimilarities. This idea was developed in detail before to calculate the ternary ($g_T$) corrections to $\lambda$ and $Y$, showing that in fact these dissimilarities make an important contribution.[15] For some systems, they may be the only source of $g_T$ corrections. In other systems, the deviations from FH behavior due to specific interactions may be an additional contribution to the corrections.[8,18]

Recently, it has been shown that an empirical relationship exists between $g_T{}^\circ$, $(\partial g_T/\partial\phi_3)^\circ$, and the liquid mixture interaction parameter, $g_{12}$.[19,20] (1 and 2 = liquids; 3 = polymer; degree sign = dilute solution values). Six different systems of the polymers PS, PMMA, and PDMS were studied. For those systems, enough data are available to determine all three quantities involved in the correlation: $g_{12}$ is obtained from $G^E$ of the liquid mixture, $g_T{}^\circ$ from $\lambda$, and $(\partial g_T/\partial\phi_3)^\circ$ from $A_2$. Careful analysis of the experimental data showed that in each one of the systems

$$\frac{g_T{}^\circ}{g_{12} + (\partial g_T/\partial\phi_3)^\circ} = K \quad (2)$$

**Table I**
**Characteristic Parameters for Polymers and Solvents**[a]

| | $T^*$, K | $p^*$, J·cm$^{-3}$ | $\tilde{V}$ | $s$, Å$^{-1}$ | $\partial \ln V/\partial \ln T$ |
|---|---|---|---|---|---|
| PS | 7420 | 547 | 1.153 | 0.47 | |
| PMMA | 7380 | 455 | 1.153 | 0.53 | |
| PDMS | 5494 | 342 | 1.225 | 0.60 | |
| benzene | 4709 | 627 | 1.292 | 0.99 | 0.365 |
| cyclohexane | 4720 | 531 | 1.291 | 0.93 | 0.363 |
| *n*-heptane | 4670 | 430 | 1.289 | 1.01 | 0.373 |
| *n*-undecane | 5240 | 442 | 1.240 | 0.94 | 0.286 |
| $CCl_4$ | 4697 | 569 | 1.293 | 0.96 | 0.366 |
| butyl chloride | 4673 | 422 | 1.295 | 0.98 | 0.370 |
| methyl ethyl ketone | 4547 | 587 | 1.300 | 1.14 | 0.385 |
| ethyl acetate | 4432 | 662 | 1.322 | 1.05 | 0.414 |
| acetonitrile | 4449 | 448 | 1.320 | 1.08 | 0.411 |
| methanol | 4772 | 500 | 1.285 | 0.99 | 0.355 |

[a] At 25 °C; refs 23–27.

is a constant independent of solvent composition over the whole range of compositions $0 \leqslant \phi_1{}^\circ \leqslant 1$. (See Figure 4 of ref 19.) The empirical values found for constant $K$ are 0.33–0.48, depending on the system.[19] This finding of constant $K$ is an empirical fact independent of any theory, because $g_{12}$, $g_T{}^\circ$, and $(\partial g_T/\partial \phi_3)^\circ$ are determined solely from experiment (each from a different measured property).

The purpose of this note is to show that the existence of such a constant $K$ and also the range of values obtained for it from experiment are predicted by the FPP theory of $\lambda$ and $Y$.

The FPP equations for $\lambda$ and $Y$ are rather lengthy. They have been applied to practical problems only in a simplified version. So, their full predictive power has not yet been put to test. But, even with the more simplified version of them, the predictions are remarkably useful. According to the simplified version (called set A of approximations in ref 15), $g_T{}^\circ$ and $(\partial g_T/\partial \phi_3)^\circ$ are given by[15,21]

$$g_T{}^\circ = [1 - (\tilde{V}_1/\tilde{V}_3)(s - \alpha)]g_{12}$$

$$(\partial g_T/\partial \phi_3)^\circ = [1 - 2(\tilde{V}_1/\tilde{V}_3)(s - \alpha) + (\tilde{V}_1/\tilde{V}_3)^2(s^2 - \alpha - s\alpha)]g_{12} \quad (3)$$

so that the theory predicts for $K$

$$K = \tfrac{1}{2}\left[1 + \frac{1}{2}\,\frac{(\tilde{V}_1/\tilde{V}_3)^2(s^2 - \alpha' - s\alpha)}{1 - (\tilde{V}_1/\tilde{V}_3)(s - \alpha)}\right]^{-1} \quad (4)$$

($\tilde{V}_i = V_i/V_i{}^*$; $s = s_3/s_1$, with $s_i$ surface to volume ratio; $\alpha = [(\partial \ln V_1)/(\partial \ln T)](p_3{}^*/p_1{}^*)(1 - T_1{}^*/T_3{}^*)$; $\alpha' = (p_3{}^*/p_1{}^*)\alpha$). In eq 3 and 4, subscript 1 denotes the mixed-solvent properties. Usually, they are taken as average values of the two liquids.

Let us analyze the predictions of eq 3 and 4. If there were no dissimilarities in contact surface and in free volume between polymer and solvents, then $\tilde{V}_1 = \tilde{V}_3$, $s_3 = s_1$, and $T_1{}^* = T_3{}^*$, and one would get $g_T{}^\circ = 0$ and $K = 0$ and the ternary effects would vanish. On the other extreme, if such dissimilarities were so large that $s^2 - \alpha' - s\alpha = 0$,[22] then eq 3 and 4 predict that $K$ would reach the value $K = 0.5$. The empirical values found for $K$ (0.33–0.48) are closer to this $K = 0.5$ limit than to $K = 0$, indicating the importance these dissimilarities play in real systems.

The values of $T_i{}^*$, $p_i{}^*$, $\tilde{V}_i$, $s_i$, and $(\partial \ln V_1)/(\partial \ln T)$, corresponding to the polymers PS, PMMA, and PDMS and to typical solvents, are shown on Table I. These values are used in eq 3 and 4 to calculate $g_T{}^\circ$, $(\partial g_T/\partial \phi_3)^\circ$, and constant $K$, predicted by FPP theory. The results for for a few polymer–mixed solvent sample systems are shown on Table II. We can see that the range of calculated $K$'s (0.36–0.49) is practically the same as covered by experiment (0.33–0.48). Thus, the FPP theory adequately predicts the constancy of $K$ and also its range of values. For polymers having low surface to volume ratios, $s$, and high characteristic temperatures, $T^*$, the values calculated are in the upper part of the range (close to 0.5).

**Table II**
**Ternary Interaction Parameter and Constant $K$ Predicted by Equations 3–4 for Some Polymer–Mixed Solvent Systems**

| | system[a] | $g_T{}^\circ/g_{12}$ | $(\partial g_T/\partial \phi_3)^\circ/g_{12}$ | $K$ |
|---|---|---|---|---|
| 1 | PS/Ch + EtOAc | 0.62 | 0.28 | 0.48 |
| 2 | PS/Bz + Ch | 0.59 | 0.26 | 0.47 |
| 3 | PS/Bz + MEK | 0.65 | 0.33 | 0.49 |
| 4 | PMMA/MeCN + BuCl | 0.59 | 0.21 | 0.49 |
| 5 | PMMA/MeCN + $CCl_4$ | 0.56 | 0.23 | 0.45 |
| 6 | PMMA/Bz + MeOH | 0.52 | 0.22 | 0.42 |
| 7 | PDMS/Hep + MEK | 0.45 | 0.20 | 0.38 |
| 8 | PDMS/Und + MEK | 0.43 | 0.18 | 0.36 |
| 9 | PDMS/Ch + MEK | 0.42 | 0.17 | 0.36 |

[a] Abbreviations: Ch, cyclohexane; Bz, benzene; Hep, heptane; Und, undecane.

Although the range of $K$ values covered by experiment is adequately predicted by the FPP theory, however, some differences arise in the system-by-system comparison. Thus, the experimental $K$ values given in ref 19 are 0.48, 0.33, 0.46, 0.40, 0.46, and 0.43, corresponding to the systems 1, 2, 4, 5, 7, and 8 of Table II. The differences between calculated and experimental values are 0.00, 0.14, 0.03, 0.05, −0.08, and −0.07, respectively. Thus, the quality of the agreement varies from system to system, but overall it is good.

In conclusion, the empirical correlation found for the ternary interaction parameter (eq 2) can be well explained by the FPP theory.

**Registry No.** PS, 9003-53-6; PMMA, 9011-14-7; C, 110-82-7; B, 71-43-2; MEK, 78-93-3; Hep, 142-82-5; Und, 1120-21-4; EtOAc, 141-78-6; BuCl, 109-69-3; $CCl_4$, 56-23-5; MeOH, 67-56-1; MeCN, 75-05-8.

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# Evolution of Polyurethane Gel Fraction near the Gelation Threshold

D. DURAND, F. NAVEAU, and J. P. BUSNEL

*Laboratoire de Chimie et Physico-Chimie Macromoléculaire, Unité associée au C.N.R.S., Université du Maine, Route de Laval, 72017 Le Mans, Cedex, France*

M. DELSANTI* and M. ADAM

*Service de Physique du Solide et de Résonance Magnétique, CEN-CEA Saclay, 91191 Gif-sur-Yvette Cedex, France.*

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The gelation process by polycondensation leading to polyurethane gels was studied below and near the gel point. The growth process of clusters was investigated by light scattering[1] and small-angle neutron scattering.[2] Mass distribution and weight-average molecular weight, near the gel point, are found to follow power laws with exponents $\tau = 2.2 \pm 0.04$ (ref 2) and $\gamma = 1.71 \pm 0.06$ (ref 1), respectively. Thus, below the gel point the growth process of branched polymers is described by percolation theory.[3,4]

The experiments reported here are performed beyond the gel point. We are interested in the evolution of the gel fraction as a function of the reaction extent $p$ and as a function of the distance $\epsilon$ to the gel point: $\epsilon = p - p_c$, $p_c$ being the reaction extent at the gel point.

Near the gel point, the gel fraction $G$, which represents the probability that a monomer belongs to the infinite cluster, increases with $\epsilon$ following a power law[5]

$$G \sim \epsilon^\beta \qquad (1)$$

The exponent $\beta$ is related to the exponents $\tau$ and $\gamma$:

$$\beta = \gamma(\tau - 2)/(3 - \tau) \qquad (2)$$

Percolation theory[5] predicts $\beta = 0.43$ ($\tau = 2.2$, $\gamma = 1.74$) and the classical mean field theory of gelation, introduced by Flory–Stockmayer,[6,7] gives $\beta = 1$ ($\tau = 2.5$, $\gamma = 1$).

Flory and Stockmayer theories lead to similar results only near the gel point. Following Flory's approach[6] $G$ must increase with $\epsilon$ as

$$G = 4\epsilon(3 + 4\epsilon^2)/(1 + 2\epsilon)^3 \qquad \text{for} \quad 0 \leqslant \epsilon \leqslant 1 - p_c \; (3)$$

Polyurethane samples were prepared without solvent in the presence of catalyst (dibutyltin dilaurate) by condensation of hydroxyl groups belonging to trifunctional units (poly(oxypropylenetriol) with molecular weight of 700) and isocyanate groups belonging to difunctional units (hexamethylene diisocyanate). The stoichiometric ratio, defined as $p = [\text{NCO}]/[\text{OH}]$ where [NCO] and [OH] are the concentrations of NCO and OH groups present initially, is determined by weighing. If $p < 1$, at complete reaction, $p$ is proportional to the number of OH groups which have reacted and is taken as the reaction extent. The verification of the absence of NCO groups at complete reaction has been described in a previous paper.[8]

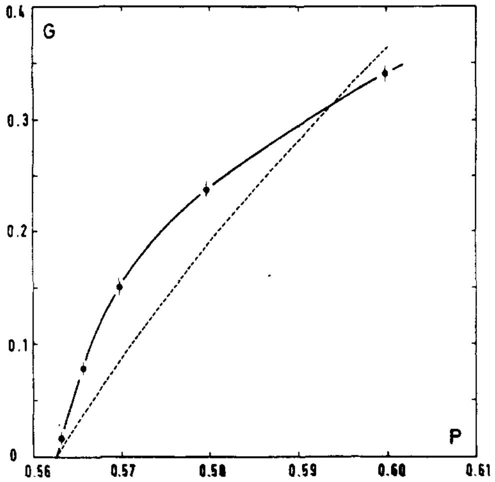

**Figure 1.** Evolution of the gel fraction $G$ as a function of the extent of reaction $p$ (linear scale). The solid line is a guide for the eye. The dashed line represents the evolution of the gel fraction according to Flory's expression (relation 3 with $p_c$ = 0.5624).

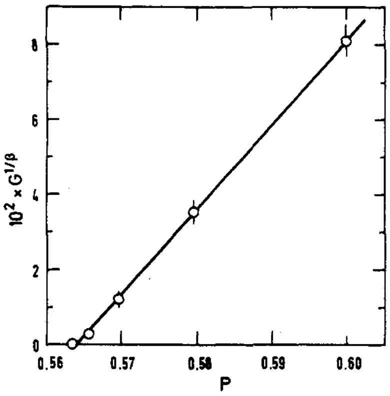

**Figure 2.** Exponent $\beta$ (=0.43) determined from $\tau$ and $\gamma$ exponent values measured below the gel point (1) accounts for the gel fraction measured beyond the gel point: $G^{1/\beta}$ is a linear function of the extent of reaction $p$.

Sol extractions were performed in the following way: a polyurethane sample (≈7 g) was put into a porous capsule, large enough (≈40 cm$^3$) to allow a complete swelling of the gel. In order to extract the soluble polymers through the porous membrane, the capsule was introduced into a closed container holding 100 cm$^3$ of good solvent tetrahydrofurane (THF). Then, after 2 days, the solution of extracted polymers in THF was removed, THF was evaporated under reduced pressure at 30 °C, and polymer clusters were weighted. This operation was repeated several times until the weight of total extracted polymers became a constant within about $10^{-3}$ g. The mass fraction of gel is calculated by difference between the mass of the extracted clusters and the total mass of the sample. The stoichiometric ratio $p$ and the corresponding gel fraction measured are given in Table I.

**Table I**
**Experimental Stoichiometric Ratio $p$ and Mass Fraction of Gel $G$**

| | | | | | | |
|---|---|---|---|---|---|---|
| $p^a$ | 0.5617 | 0.5632 | 0.5656 | 0.5695 | 0.5796 | 0.5999 |
| $G$ | 0 | 0.016 ± 0.005 | 0.078 ± 0.006 | 0.150 ± 0.007 | 0.237 ± 0.007 | 0.339 ± 0.007 |

[a] The precision on $p$ is $10^{-4}$.