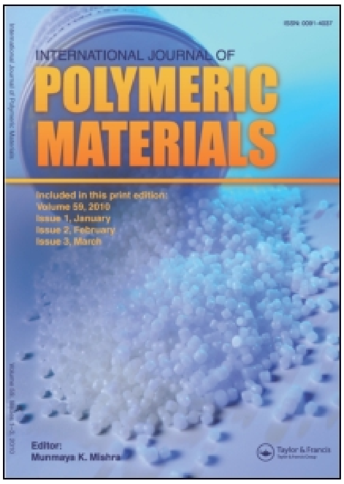

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

# Preferential Solvation. Effect on Polymer Dimensions

A. Dondos[a]; H. Benoit[b]
[a] Laboratory of Physical Chemistry, University of Athens, Athens, Greece [b] Centre de Recherches sur les Macromolécules (CNRS), Strasbourg, France

**To cite this Article** Dondos, A. and Benoit, H.(1976) 'Preferential Solvation. Effect on Polymer Dimensions', International Journal of Polymeric Materials, 4: 3, 175 — 193

**To link to this Article: DOI:** 10.1080/00914037608072378

**URL:** http://dx.doi.org/10.1080/00914037608072378

*Intern. J. Polymeric Mater.*, 1976, Vol. 4, pp. 175–193

Printed in Reading, England

# Preferential Solvation. Effect on Polymer Dimensions†

A. DONDOS

*Laboratory of Physical Chemistry, University of Athens, Athens, Greece*

and

H. BENOÎT

*Centre de Recherches sur les Macromolécules (CNRS), 67083 Strasbourg, France*

(*Received August 20, 1973*)

In this paper we discuss the light scattering theory of preferential solvation. We also present a more recent theory predicting a preferential solvation dependence on polymer molecular weight. These theories have been confirmed by the experimental results of the present work. It was established that the polymer coil dimensions depend on the local solvent composition and not on the analytical one. The local solvent composition can be calculated, in certain cases, from the value of the preferential solvation coefficient.

## 1 INTRODUCTION

Many researchers have studied polymers in binary solvent systems from both theoretical and phenomenological point of view. Their published works concern either the dimensions of macromolecules in solution,[1–5] or the preferential solvation of one component of the solvent system into the macromolecular coil.[6–12] The present communication connects these two areas of investigation, namely the preferential solvation and the dimensions of the macromolecule. Our objective is to explain the experimentally measured dimensions of the macromolecules dissolved in a binary system, based not only on the thermodynamic parameters of the two components of the solvent, but also on the preferential solvation which takes place in such systems.

The most important methods of investigating the preferential solvation are

---

†Presented at the Midland Macromolecular Meeting on "Order in Polymer Solutions", August 20–24, 1973.

proton relaxation,[13,14] differential refractometry[11,15,16] and light scattering.[7,10,12] In our present work, the experimental results were derived from light scattering measurements. The dimensions of macromolecular chains will be expressed in terms of intrinsic viscosity $[\eta]$ throughout this work ($[\eta]$ in $cm^3/g$).

In the second part, a brief review of the theory of the light scattering of polymers dissolved in a binary solvent system and the relation between the preferential solvation and the polymer dimensions will be given. In the third part we shall present some experimental results confirming the theoretical predictions.

## 2 THEORETICAL

### 2.1 Light scattering in ternary systems polymer-two solvents

The Debye's molecular theory[17] which treats the situation in binary systems (one polymer in one solvent) gives the following well-known equation for the difference of the Rayleigh ratios $R - R_0$ between the solution and the pure solvent (for the scattering angle 90°)

$$R - R_0 = 8(\pi/\lambda)^4\, Np^2/E^2 \tag{1}$$

where $\lambda$ is the wavelength of the incident light, **E** the electric field of the incident beam, **p** is the dipole moment of the macromolecule which behaves as a dipole under the influence of the above field and $N$ is the number of molecules of the solute per unit volume.

For a dilute solution of the polymer we have

$$\mathbf{p} = (\mathbf{P} - \mathbf{P}_0)/N \tag{2}$$

where **P** and $\mathbf{P}_0$ are the polarization of the solution and pure solvent, respectively. According to the Maxwell's theory we get

$$\mathbf{p} = (4\pi N)^{-1}(\tilde{n}^2 - \tilde{n}_0^2)\mathbf{E} \tag{3}$$

where $\tilde{n}$ and $\tilde{n}_0$ are the refractive indices of the solution and pure solvent, respectively. Combination of Eqs. (1) and (3) gives

$$R - R_0 = \tfrac{1}{2}\pi^2(\tilde{n} - \tilde{n}_0)^2(\tilde{n} + \tilde{n}_0)^2/(N\lambda^4)$$

Assuming that $\tilde{n} + \tilde{n}_0 \approx 2\tilde{n}_0$ and $\tilde{n} - \tilde{n}_0 \approx c(d\tilde{n}/dc)$ where $c$ is the polymer concentration and $d\tilde{n}/dc$ the refractive index increment of the solution, the above relation becomes

$$R - R_0 = 2\pi^2\tilde{n}_0^2c^2(d\tilde{n}/dc)^2/(N\lambda^4)$$

Since $c/N = M/\mathbf{N}_A$ where $\mathbf{N}_A$ is the Avogadro number and $M$ is the molecular weight of the polymer, we get

$$R - R_0 = \frac{2\pi^2\tilde{n}_0{}^2}{\lambda^4\mathbf{N}_A}\left(\frac{d\tilde{n}}{dc}\right)^2 cM \tag{4}$$

The above relation which holds for the binary systems has been modified by Strazielle and Benoît[7] in 1961 to be applicable also for ternary systems (one polymer—two solvents).

Let us suppose that during the dissolution of a polymer in a mixture of two solvents, $\gamma_1$ molecules of the solvent 1 are absorbed in excess per macromolecular chain. These $\gamma_1$ molecules should correspond to $\gamma_2$ molecules of the solvent 2 which move away from the chain, so we shall have

$$\gamma_1\bar{V}_1 = \gamma_2\bar{V}_2 \tag{5}$$

where $\bar{V}_1$ and $\bar{V}_2$ are the partial molar volumes of the solvent 1 and 2, respectively.

If the initial composition of the mixture of the solvents (*analytical* composition) is $N_1$ molecules of the solvent 1 and $N_2$ molecules of the solvent 2 per cm$^3$, the polarization $\mathbf{P}_0$ of the solvent should be equal to

$$\mathbf{P}_0 = N_1\mathbf{p}_1 + N_2\mathbf{p}_2 \tag{6}$$

Thus Eq. (2) becomes

$$\mathbf{p} = (\mathbf{P} - N_1\mathbf{p}_1 - N_2\mathbf{p}_2)/N \tag{7}$$

The above relation, however, holds only in the case where there is no preferential solvation. If we take now into account the preferential solvation, the scattering heterogeneity will no longer consist of the dissolved molecule alone, but of this molecule with the $\gamma_1$ absorbed molecules 1 and the $\gamma_2$ removed molecules 2. So the polarization of the solvent will be given not by the relation (6) but by the following formula:

$$\mathbf{P}_0' = (N_1 - \gamma_1')\mathbf{p}_1 + (N_2 + \gamma_2')\mathbf{p}_2$$

where $\gamma_1'$ and $\gamma_2'$ are the number of molecules of solvents 1 and 2 per unit volume, respectively, which are coupled with the polymer or taken away from the polymer. In the case of two solvents, Eq. (2) becomes

$$\mathbf{p}' = (\mathbf{P} - N_1\mathbf{p}_1 - N_2\mathbf{p}_2 + \gamma_1'\mathbf{p}_1 - \gamma_2'\mathbf{p}_2)/N$$

Finally, from Eq. (7) and relations $\gamma_1'/N = \gamma_1$ and $\gamma_2'/N = \gamma_2$ we get

$$\mathbf{p}' = \mathbf{p} + \gamma_1\mathbf{p}_1 - \gamma_2\mathbf{p}_2 \tag{8}$$

We notice that Eq. (8) gives correctly the dipole moment of the macromolecule even in the case of a mixed solvent showing no preferential solvation.

The difference of the Rayleigh ratios is now obtained by substituting $\mathbf{p}'$ of

Eq. (8) for **p** in Eq. (1), also using Eqs. (3) and (5) and the aforementioned approximations

$$R - R_0 = \frac{8\pi^4}{\lambda^4}\frac{c\mathbf{N}_A}{M}\left[\frac{\tilde{n}_0 M}{2\pi \mathbf{N}_A}\frac{d\tilde{n}}{dc} + \frac{\gamma_1}{E}\left(p_1 - \frac{\bar{V}_1 p_2}{\bar{V}_2}\right)\right]^2 \tag{9}$$

We note again that $\tilde{n}_0$ is the refractive index of the mixture of the two solvents. For this mixture we have

$$(\tilde{n}_0^2 - 1)\mathbf{E} = 4\pi(N_1\mathbf{p}_1 + N_2\mathbf{p}_2)$$

or, after differentiation

$$2\tilde{n}_0 d\tilde{n}_0 \mathbf{E} = 4\pi(\mathbf{p}_1 dN_1 + \mathbf{p}_2 dN_2) \tag{10}$$

Assuming now that the change of composition of the solvent mixture in the vicinity of the macromolecular chain proceeds without any change in volume, we also have

$$dN_1\bar{V}_1 = -dN_2\bar{V}_2$$

This relation combined with Eq. (10) yields the following equation

$$2\tilde{n}_0(d\tilde{n}_0/dN_1) = 4\pi E^{-1}(p_1 - p_2\bar{V}_1/\bar{V}_2)$$

which can be used to eliminate the dipole moments $p_1$ and $p_2$ from Eq. (9):

$$R - R_0 = \frac{2\pi^2\tilde{n}_0^2}{\lambda^4\mathbf{N}_A}cM\left[\frac{d\tilde{n}}{dc} + \frac{\gamma_1}{M}\mathbf{N}_A\frac{d\tilde{n}_0}{dN_1}\right]^2 \tag{11}$$

If the number of molecules $N_1$ is expressed in terms of the volume fraction $\phi_1$, $N_1 = \phi_1\mathbf{N}_A/\bar{V}_1$, the above relation becomes

$$R - R_0 = \frac{2\pi^2\tilde{n}_0^2}{\lambda^4\mathbf{N}_A}cM\left[\frac{d\tilde{n}}{dc} + \frac{\gamma_1}{M}\bar{V}_1\frac{d\tilde{n}_0}{d\phi_1}\right]^2 \tag{12}$$

where $d\tilde{n}_0/d\phi_1$ is the change of the refractive index of the mixture of the two solvents caused by a change in the composition $\phi_1$ of the mixture.

To compare Eq. (12) with the relation (4) which gives the molecular weight of the polymer in the case of a single solvent, we can write Eq. (12) as

$$R - R_0 = \frac{2\pi^2}{\lambda^4}\frac{\tilde{n}_0}{\mathbf{N}_A}\left(\frac{d\tilde{n}}{dc}\right)^2 cM_{\text{app}} \tag{13}$$

where

$$M_{\text{app}} = M\left[1 + \frac{\gamma_1}{M}\bar{V}_1\left(\frac{d\tilde{n}_0}{d\phi_1}\Big/\frac{d\tilde{n}}{dc}\right)\right]^2 \tag{14}$$

is the apparent molecular weight of the polymer determined in the solvent mixture.

Defining the coefficient of preferential solvation $\lambda'$ as

$$\lambda' = \gamma_1\bar{V}_1/M \tag{15}$$

we get

$$\lambda' = \left[\left(\frac{M_{\mathrm{app}}}{M}\right)^{\frac{1}{2}} - 1\right]\left(\frac{d\tilde{n}}{dc}\Big/\frac{d\tilde{n}_0}{d\phi_1}\right) \tag{16}$$

The coefficient of preferential solvation $\lambda'$ represents the excess volume of solvent 1 which has been absorbed per unit mass of the polymer. Knowing the actual molecular weight of the polymer $M$, the coefficient of preferential solvation can be calculated from $M_{\mathrm{app}}$ determined in the mixture of the two solvents using relation (16).

The basic relation in the work of Strazielle and Benoît [Eq. (11) of this paper] is similar to the equation proposed by Ewart *et al.*[6] However, Strazielle and Benoît give a more precise signification of the coefficient of the preferential solvation.

It is obvious that the usefulness of Eq. (16) for the determination of preferential solvation is restricted to the mixtures of solvents having different refractive indices, so that $d\tilde{n}_0/d\phi_1 \neq 0$.

## 2.2 Dependence of the preferential solvation on the molecular weight

Many published studies on the preferential solvation of polymers dissolved in a binary solvent system do not show any dependence of preferential solvation on the molecular weight of the polymer. We mention the work of Strazielle and Benoît[7] and the work of Okita and co-workers.[16] This lack of dependence can be explained today by the fact that the polymer samples used in these studies did not have a low enough molecular weight. As we shall see later, this dependence becomes experimentally detectable only for molecular weights lower than 50,000.

Assuming that the preferential solvation concerns only the immediate vicinity of the chain—and this assumption was made by many researchers—it is difficult to explain the dependence of the preferential solvation on the polymer molecular weight. However, it has been shown[18] that, near the theta conditions, the preferential solvation concerns the whole volume occupied by the polymer coil. Inside this volume, the *local* composition of the solvent system is different from the initial composition before the polymer was added, referred to as the *analytical* composition or *bulk* composition. This bulk composition can be assumed as representing the composition of the binary solvent system in the space between the macromolecular coils. The difference between the local and the bulk composition which is due to the preferential solvation, justifies a concept of *two* theta conditions: the inter- and intramolecular theta conditions. When, for a given bulk composition, the second virial coefficient becomes zero, the macromolecular chains exhibit an expansion coefficient $\alpha$ greater than unity. This is a consequence of the fact that inside the polymer coil, the local composition is richer in "good" solvent.

As mentioned before, this phenomenon is observed near the theta-point where the number of repeat units per unit volume is relatively high. This led us to the investigation of the effect of repeat-unit density, $\rho$, on the preferential solvation. As it is known, this density $\rho$ changes with the molecular weight and it becomes very high for the low molecular weight chains.

The mean coefficient of preferential solvation $\langle\lambda'\rangle$ is calculated as a normalized sum of all preferential solvation coefficients for each repeat unit[10]

$$\langle\lambda'\rangle = (1/X)\int_0^X \lambda' dx \tag{17}$$

where $X$ is the total number of repeat units in the chain. It is also considered that the preferential solvation coefficient $\lambda'$ depends on the repeat-unit density $\rho$ and this dependence is expressed by the following relation

$$\lambda' = \lambda'_\infty + a\rho \tag{18}$$

where $\lambda'_\infty$ represents the value of preferential solvation coefficient for an infinite chain, and $a$ is a constant. Consequently, the mean experimental value of the coefficient is given by

$$\langle\lambda'\rangle = (1/X)\int_0^X (\lambda'_\infty + a\rho)dx = \lambda'_\infty + (a/X)\int_0^X \rho dx \tag{19}$$

Assuming that the distribution of repeat-unit density around the macromolecular coil center of mass is gaussian[19]

$$\rho = X(3/2\pi\langle R^2\rangle)^{3/2}\exp(-3r^2/2\langle R^2\rangle) \tag{20}$$

where $r$ is the distance from the center of mass and $\langle R^2\rangle$ the mean square radius of gyration, the integration along the chain, Eq. (19), can be replaced by a weighted integration over the volume

$$\langle\lambda'\rangle = \lambda'_\infty + (a/X)\iiint \rho^2 dV$$

Substituting $\rho$ from Eq. (20), we obtain, after integration

$$\langle\lambda'\rangle = \lambda'_\infty + a(3/4\pi)^{3/2}X\langle R^2\rangle^{-3/2}$$

Knowing that

$$\langle R^2\rangle = b^2X\alpha^2$$

where $b$ is the length of a repeat unit and $\alpha$ the expansion coefficient, we obtain

$$\langle\lambda'\rangle = \lambda'_\infty + a(3/4\pi b^2)^{3/2}/(X^{\frac{1}{2}}\alpha^3)$$

But $X$ is proportional to the molecular weight, so we have:

$$\langle\lambda'\rangle = \lambda'_\infty + AM^{-\frac{1}{2}}\alpha^{-3}$$

Near the theta point where $\alpha \simeq 1$, the above relation becomes

$$\langle \lambda' \rangle = \lambda'_{\infty} + AM^{-\frac{1}{2}} \tag{21}$$

This is the relation between the preferential solvation coefficient $\langle \lambda' \rangle$ and the molecular weight near the theta point.

Evidently, a plot of $\langle \lambda' \rangle M^{\frac{1}{2}}$ versus $M^{\frac{1}{2}}$ should give a straight line, according to the above theoretical relation (21). As we will see later, this is indeed the case in many polymer-binary solvent systems.

Read[8] as well as Živný, Pouchlý and Šolc[20] predicted theoretically the dependence of the preferential solvation on the molecular weight. Since these authors investigated experimentally only high molecular weight polymers and did not find any dependence of $\langle \lambda' \rangle$ on the molecular weight they dismissed the molecular weight dependent term as unimportant.

## 2.3 Preferential solvation effect on molecular dimensions

As we have seen, the preferential solvation changes the binary solvent composition in the vicinity of the macromolecular chain, and in certain cases, this change in composition affects the entire volume of the random polymer coil. It was judged worth studying the effect of solvent composition on the macromolecular dimensions.

Theoretically, the preferential solvation can affect the molecular dimensions in the following ways:

a) First of all, the change of the solvent composition in the vicinity of the polymer chain must affect the unperturbed dimensions of the chain. The environment of the repeat units of the chain is the local composition of the solvent, as it is dictated by the preferential solvation, and this composition is different from the analytical or bulk composition.[21] (We assume now that the change of solvent composition concerns only the vicinity of polymer chains.)

If the coefficient of preferential solvation is known, one can calculate the number of excess molecules of the solvent 1, $\gamma_1$, in the vicinity of the chain from Eq. (15). Consequently, one can also calculate the number $\gamma_2$ of the molecules of the solvent 2 which have been displaced: from Eqs. (5) and (15), we have

$$\gamma_1 \bar{V}_1 = \gamma_2 \bar{V}_2 = \langle \lambda' \rangle M = \langle \lambda' \rangle mX \tag{22}$$

where $X$ is the number of repeat units in the chain and $m$ is the molecular weight of a repeat unit.

Let us call $Z$ the number of molecules of solvent components per repeat unit of the chain. Along the chain and in the vicinity of the chain, the correct number of molecules of species 1 and 2 will be $XZx_1 + \gamma_1$ and $XZx_2 - \gamma_2$, where $x_1$ and $x_2$ are the molar fractions of solvents 1 and 2, according to the analytical composition. Assuming now that the molar volumes $\bar{V}_1$ and $\bar{V}_2$ are sufficiently close (so that one can take the same value of $Z$ for both solvents surrounding the chain), the actual molar fraction $x_1'$ of solvent 1 in the vicinity of the chain is given by

$$x_1' = \frac{XZx_1 + \gamma_1}{XZx_1 + \gamma_1 + XZx_2 - \gamma_2}$$

and, introducing Eq. (22), we obtain

$$x_1' = \frac{Zx_1 + \langle\lambda'\rangle(m/\bar{V}_1)}{Z + \langle\lambda'\rangle[(m/\bar{V}_1) - (m/\bar{V}_2)]} \tag{23}$$

This equation gives the local composition of the solvent near the macromolecular chain. If the binary solvent composition has any effect on the unperturbed dimensions, one should take into consideration not the analytical but the local composition as given by the above relation. The choice of $Z$ value is of fundamental importance. For low values of $Z$ one finds that, near the theta point, the chain is surrounded almost exclusively by good solvent molecules ($x_1' \to 1$). As will be seen later, many experimental results point to the need of using the local composition given by Eq. (23) when determining the unperturbed dimensions, instead of the analytical composition.

b) It is mentioned earlier that, near the theta point, the preferential solvation alters the composition of the solvent system throughout the entire volume "occupied" by the polymer coil. Under these conditions, the macromolecular dimensions, in general, are a function of the preferential solvation, because the latter determines the solvent composition inside the polymer coil. Qualitatively we can state that, near the intermolecular theta point and for high preferential solvation of the good solvent, the polymer chain exhibits larger dimensions, as compared to the case of low preferential solvation.

c) For relatively low molecular weight chains the preferential solvation is higher near the theta point, compared to the high molecular weight chains, all other factors being the same. Therefore one should expect a greater chain expansion of the low molecular weight chains. This of course could not be so, if the preferential solvation were independent of the molecular weight of the chain.

d) Finally, the preferential solvation can affect the macromolecular dimensions even under conditions far away from the theta point. This is based on the assumption that when the thermal motion brings two distant repeat units of a chain close to each other, their interaction will be dominated only by the *local* solvent composition, even though these units may have travelled, prior to their encounter, through domains of different solvent composition. Therefore, through the change of local composition, the preferential solvation affects the long-distance interaction of the repeat units which, in turn, affects the macromolecular dimensions.

Our experimental results, presented below, are in agreement with these assumptions.

## 3 EXPERIMENTAL RESULTS

### 3.1 Dependence of the preferential solvation on the polymer molecular weight

The coefficient of preferential solvation $\langle\lambda'\rangle$ was determined for some ternary systems.[10] The determination was based on light scattering measurements as proposed by Strazielle and Benoît [Eq. (16)]. Here we present our results for the following two systems: (a) polystyrene/benzene/methanol; (b) polystyrene/carbon tetrachloride/methanol.

The light scattering measurements were performed at 25°C with a photogoniodiffusimeter FICA. All polystyrene (PS) samples were prepared by anionic polymerization at $-70$°C, therefore we can assume that they contain only linear chains. Most of the samples were fractionated in order to bring the polydispersity index of all used samples below 1.2.

The numerical data for the above two systems are reported in Ref. 10.

Figure 1 represents the dependence of $\langle\lambda'\rangle$ as a function of molecular weight. The coefficient $\langle\lambda'\rangle$ decreases with increasing molecular weight down to a limit, corresponding to the molecular weight of approximately 100,000. Beyond this molecular weight, the value of coefficient $\langle\lambda'\rangle$ remains practically constant.

In the same figure, the dependence of $\langle\lambda'\rangle$ is given also for non-theta conditions (mixture of two liquids, behaving as a good solvent). In this case we see that there is no increase of $\langle\lambda'\rangle$ for the low molecular weight fractions. This is in good agreement with the predictions of the theory, namely that the effect of the density $\rho$ (number of repeat units per unit volume) on the preferential solvation becomes significant only for high $\rho$ values, or near theta conditions.

Figure 2 shows a plot of $\langle\lambda'\rangle M^{\frac{1}{2}}$ as a function of $M^{\frac{1}{2}}$ for the same three systems as in Figure 1. According to Eq. (21), the coordinate systems of Figure 2 must produce straight lines with the slope $\lambda'_{\infty}$ and the intercept equal to the coefficient $A$. We notice that the experimental points fall indeed on a straight line, confirming the proposed relation. Below a certain concentration in precipitant of the solvent-system (system behaving as a good solvent), there is no dependence of the preferential solvation on molecular weight and the experimental line passes through the origin.

Figure 3 presents the variation of coefficient $A$ for polystyrene in two solvent systems as a function of precipitant concentration.

There is also another confirmation of the suggested relation between the preferential solvation and the density of repeat units, based on the study of

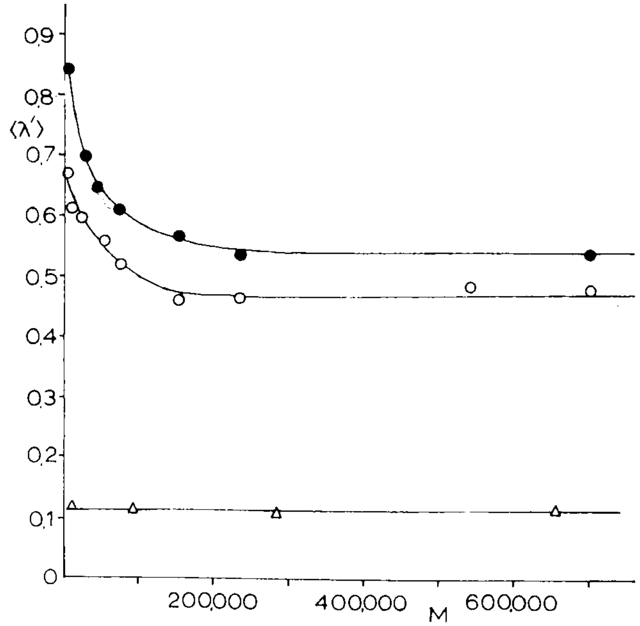

FIGURE 1 The preferential solvation coefficient for polystyrene solutions at 25°C as a function of the molecular weight in the following solvent mixtures: (●) $CCl_4$-methanol 79:21, (○) benzene-methanol 74.5:25.5, (△) $CCl_4$-methanol 95:5.

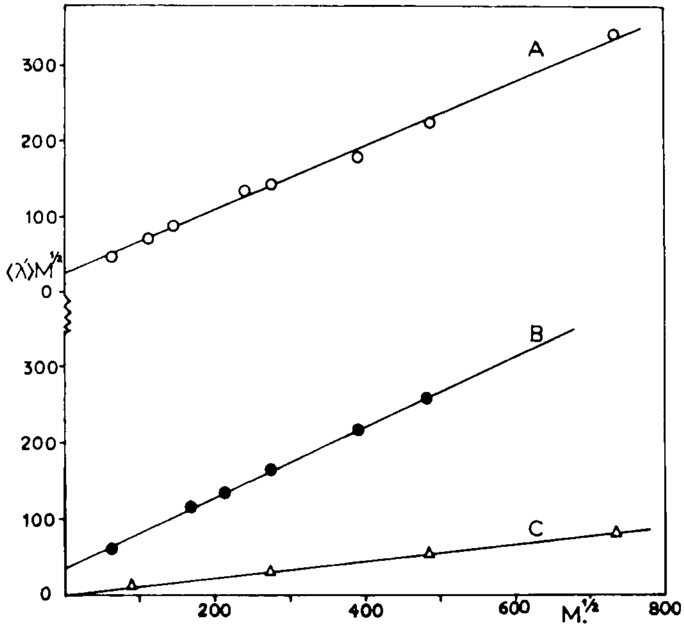

FIGURE 2 Application of Eq. (21) for polystyrene fractions in the following solvent mixtures: (A) benzene-methanol 74.5:25.5, (B) $CCl_4$-methanol 79:21, (C) $CCl_4$-methanol 95:5.

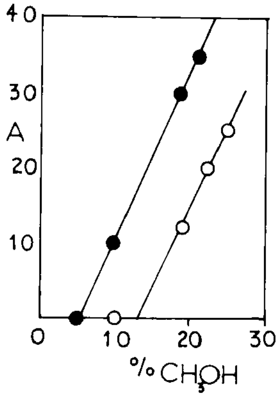

FIGURE 3 The coefficient $A$ of Eq. (21) for polystyrene as a function of the precipitant content in the mixture, for two solvent mixtures: (●) $CCl_4$–methanol, (○) benzene–methanol.

star-like polymer models. For these branched chains, we assume a higher $\rho$ value than for the linear ones of the same molecular weight. Figure 4 reproduces the results of François[22] confirming the expected higher value of $\langle\lambda'\rangle$ for a star-like polymer as compared to a linear polymer of the same molecular weight.

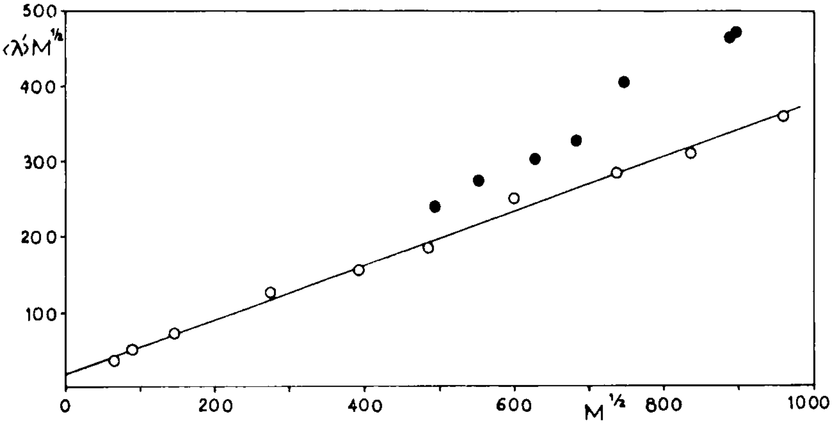

FIGURE 4 Application of Eq. (21) for polystyrene in the mixture benzene–methanol 77.8:22.2. (○) Linear polystyrene, (●) branched polystyrene.

## 3.2 Preferential solvation effect on polymer dimensions under theta conditions

We have seen earlier, that the preferential solvation changes the composition of the solvent system inside the volume occupied by the polymer coil at, or near, the theta point. The chain is embedded now in a solvent mixture, whose composition is determined by the preferential solvation and, in general, this local composition is different from that of the original solvent mixture. Evidently, this local composition is richer in good solvent. The difference between local and analytical composition leads logically to the concept of two theta conditions: one, for which the chain expansion coefficient is equal to unity (intramolecular theta conditions) and the other, for which the second virial coefficient is zero (intermolecular theta conditions).

For a polymer in various binary solvent systems behaving as "intermolecular" theta solvents, the chain expansion coefficient is the higher, the greater the preferential solvation. Elias *et al.*[23] were the first to observe that, indeed, at the theta conditions, a polymer exhibits variable molecular dimensions, depending on the nature of solvent/precipitant system. The viscosity at theta conditions ($A_2 = 0$) of the same polystyrene in benzene-methanol mixture was greater than that in dioxane-methanol mixture. Here it should be emphasized that in both cases the second virial coefficient $A_2$ was zero. Today, it is established that the preferential solvation of polystyrene in the first system is much larger than that for the second system.[24]

A more systematic study[18] has proven that in systems with $A_2 = 0$, there is a direct relation between the solvation coefficient $\langle\lambda'\rangle$ and the coefficient $B$ of the Stockmayer-Fixman equation[25]

$$[\eta]M^{-\frac{1}{2}} = K_\theta + 0{,}51\Phi_0 B M^{\frac{1}{2}} \qquad (24)$$

As known, $B$ expresses the long-range interactions of chain (and it is directly related to the expansion coefficient $\alpha$. Figure 5 shows the relation between

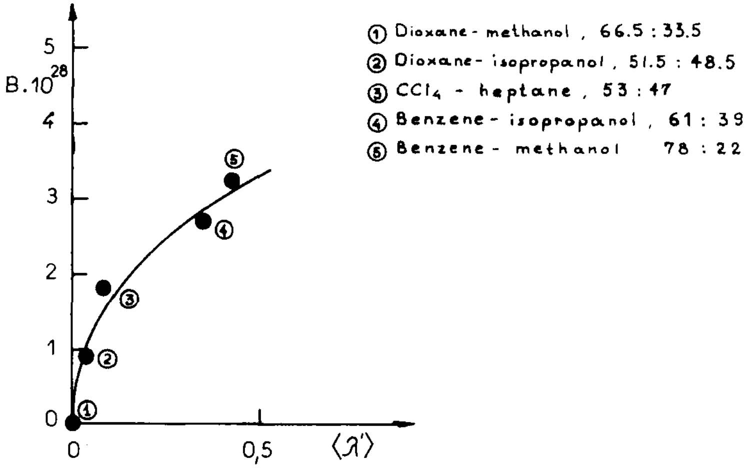

FIGURE 5 The parameter $B$ of Eq. (24) as a function of $\langle\lambda'\rangle$ at the intermolecular theta point ($A_2 = 0$).

$\langle\lambda'\rangle$ and $B$ for different systems. Apparently, in the absence of any preferential solvation ($\langle\lambda'\rangle = 0$), the analytical and local compositions are equal; therefore, if $A_2 = 0$, $B$ should be zero too.

### 3.3 Expansion of low molecular weight chains at the theta point

From Figure 1 we see that the low molecular weight chains exhibit higher value for $\langle\lambda'\rangle$, compared to the high molecular weight chains under the same conditions. The above observation can explain the fact that for the low molecular weight chains the expansion coefficient $\alpha$ is higher.

For chains of the molecular weight more than 100,000, the coefficient $\langle\lambda'\rangle$ remains almost constant and the chain expansion must be the same for all fractions. Therefore, the Stockmayer-Fixman theory can be applied. In Figure 6 we see that, indeed, the experimental points for the ternary systems A and B show a linear dependence in this region. However, for low molecular weight chains (M $<$ 100,000) the experimental points are located above the lines and their deviation is the larger the smaller the molecular weight of polystyrene fractions. Comparison of Figures 1 and 6 shows clearly the existing relationship between the preferential solvation and the macromolecular dimensions. For

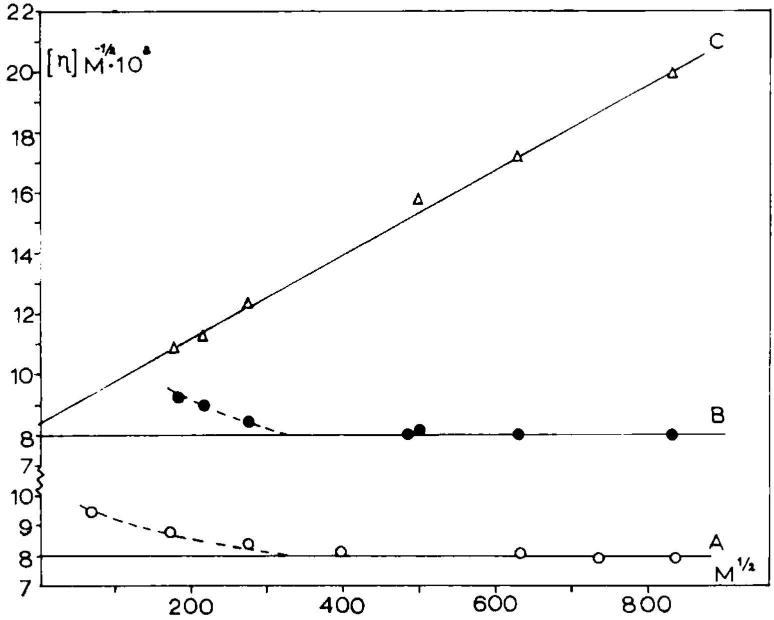

FIGURE 6 The Stockmayer–Fixman diagrams for polystyrene at 25°C in (A) benzene–methanol 74.5:25.5, (B) $CCl_4$–methanol 79:21, (C) $CCl_4$–methanol 92.5:7.5.

conditions far away from the theta point (where $\langle \lambda' \rangle$ is the same for all fractions) all the experimental points fall on the same line in the Stockmayer-Fixman diagram (Figure 6, system C).

## 3.4 Influence of the preferential solvation on the unperturbed dimensions of polymers

We have studied systematically the influence of the excess free energy of mixing of two solvents on the unperturbed dimensions of macromolecular chains dissolved in the mixture.[26,27] It has been found that there is a direct relation between the unperturbed dimensions of the polymer, expressed by the coefficient $K_\theta$ ($K_\theta = [\eta]_\theta/M^{\frac{1}{2}}$) determined in a mixture of two liquids, and the excess free energy $\Delta G^E$ of this mixture.

The unperturbed dimensions can be determined from the plot $[\eta]M^{-\frac{1}{2}}$ against $M^{\frac{1}{2}}$, according to the equation given by the Stockmayer-Fixman theory [Eq. (24)]. In our case, we neglected the low molecular weight data deviating from the linear relationship due to higher values of $\langle \lambda' \rangle$ and used only the high molecular weight fractions for extrapolation, as indicated in Figure 6. This method has been checked by us as well as by other authors (see, *e.g.*, the paper by Tanaka *et al.*[28]).

For $\Delta G^E > 0$, the $K_\theta$ value found is larger than the mean value obtained from $K_\theta$ values for pure solvents. On the other hand if $\Delta G^E < 0$, the $K_\theta$ value is smaller than the mean value.[3]

The increment of the determined unperturbed dimensions from the ideal value, obtained using the values determined in the pure solvents, is given by the difference $\Delta K_\theta$ defined as a percent increment

$$\Delta K_\theta = 100(X - 1)$$

where

$$X = K_\theta/(\phi_1 K_{\theta 1} + \phi_2 K_{\theta 2})$$

$K_\theta$, $K_{\theta 1}$ and $K_{\theta 2}$ are the values obtained in the solvent mixture and in the pure solvents 1 and 2, respectively, and $\phi_i$ are the volume fractions characterizing the composition of the solvent mixture.

We have observed that the shape of the deviation of the unperturbed dimensions does not correspond to that of $\Delta G^E$. In many cases when approaching the precipitation point of the polymer, we have noticed a decrease of $K_\theta$ in spite of the increase of $\Delta G^E$ corresponding to the analytical composition of the mixture. Many times it has been observed that at the precipitation point, the $K_\theta$ value becomes identical to that determined in the pure good solvent.

We have already explained the discrepancy between the increment of the unperturbed dimensions and that of $\Delta G^E$ corresponding to the analytical composition.[21] We derived the above relation (23) giving the composition of mixture in the vicinity of the macromolecular chain (local composition) which is different from the original composition (analytical composition).

As we have previously noticed the basic problem is the choice of the value of $Z$. We have chosen the value $Z = 3$ which is in a better agreement with our experimental data. According to the Tompa's calculations[29] the value of 3 for $Z$ is quite probable. Also the experimental results of Lange[30] give the same value for $Z$. Applying the relation (23) with $Z = 3$ and using the determined values of $\langle\lambda'\rangle$ we are in a position to give a simple relation between $\Delta K_\theta$ and $\Delta G^E$. So, when we approach the theta point we obtain $\Delta K_\theta \approx 0$ and the relation (23) gives the mole fraction of the good solvent in the vicinity of the chain, to be nearly the unity. This means that the chain is surrounded only by the molecules of the good solvent and thus the coincidence of the $K_\theta$ value at the precipitation point with that of pure solvent is obvious.

If we represent the variation of the value $\Delta K_\theta$ as function of $\Delta G^E$ which corresponds to the local composition of the mixture of solvents we obtain a straight line which passes through the origin.[21] Here we are giving only the results for the system polystyrene-benzene-methanol.

Figure 7 shows the variation of $K_\theta$ and $\langle\lambda'\rangle$ as a function of the analytical composition of the solvent mixture (mole fraction $x_1$). Table I gives the values

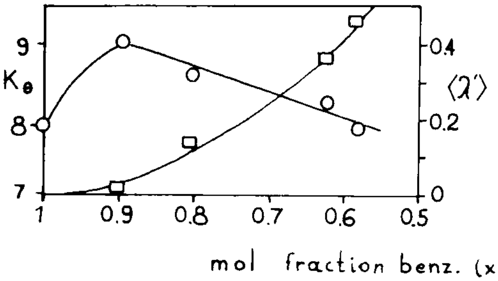

FIGURE 7 Dependence of $K\theta$ and $\langle\lambda'\rangle$ for polystyrene solutions in benzene-methanol mixture on the analytical composition of the mixture. Reprinted from Ref. (21) by courtesy of the American Chemical Society.

TABLE I

Viscometric and preferential-sorption data for the system PS–benzene–methanol

| $x_1{}^a$ | $K\theta \times 10^2$ | $\Delta K\theta\%$ | $\langle\lambda'\rangle$ | $x_1{}'^b$ | $\Delta G^E$ | $x_1{}'^c$ | $\Delta G^E$ |
|---|---|---|---|---|---|---|---|
| 1 | 7.9 | | | 1 | | 1 | |
| 0.895 | 9.0 | 12.6 | ~0 | 0.895 | 115 | 0.895 | 115 |
| 0.800 | 8.6 | 8.8 | 0.14 | 0.915 | 95 | 0.925 | 80 |
| 0.620 | 8.25 | 4.4 | 0.37 | 0.930 | 80 | 0.960 | 50 |
| 0.580 | 7.9 | 0 | 0.47 | 0.963 | 45 | ≈1 | 0 |

[a] Analytical composition.

[b] Local composition calculated from Eq. (23) with $Z = 3$.

[c] Local composition calculated from Eq. (23) with $Z = 2.8$.

of local compositions of the solvent mixture $x_1'$ for two values of $Z$ ($Z = 2.8$, $Z = 3$).

Using the values of $\Delta G^E$ corresponding to the local compositions of mixture[31] we finally obtain the straight lines of Figure 8 which is a confirmation of the proposed equation (23).

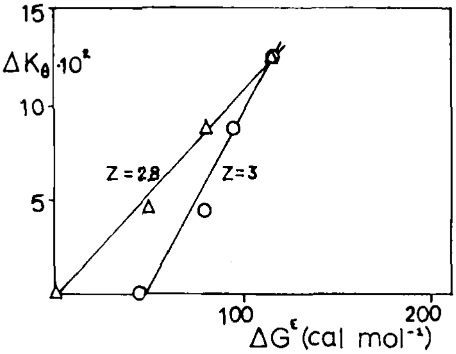

FIGURE 8 Relationship between the increment of $K_\theta$ and $\Delta G^E$ (corresponding to the local composition of the solvent mixture) for the system polystyrene–benzene–methanol and for two values of $Z$.

### 3.5 Influence of the preferential solvation on the dimensions of polymers dissolved in a mixture of good solvents

As we have mentioned in the second section of this paper, the interactions between two remote segments of a chain dissolved in a mixture of two good solvents, are through the internal space of the coil which has the same solvent composition as the analytical one. On the contrary, when the two monomer units of the chain approach each other they are surrounded by mixed solvent of local composition which exists in the vicinity of the chain. Therefore the long-range interactions depend upon the local composition of the mixture and thus on the preferential solvation.

A large number of experimental results show that in many cases the dimensions of polymers, measured in a solvent mixture and expressed by the intrinsic viscosity $[\eta]$, are higher or lower than the weighted average value for the two pure solvents. This viscosity increment is related to the value of $\Delta G^E$ of the solvent mixture, similarly as the increment of the unperturbed dimensions. Theory gives a relationship between the increment of the dimensions and the value $\Delta G^E$ but the agreement between the theoretical predictions and the experimental results is only qualitative.[3] Here, the deviations are expressed by the percent difference $\Delta[\eta]_{\mathrm{exp}}$ between the determined value of $[\eta]$ in the mixture and the weighted average value.

Unfortunately, not only the absolute magnitude of the calculated deviations but also the shape of their composition dependence does not match the experimental data.[32] Usually the maximum of the calculated curve, $\Delta[\eta]_{\mathrm{cal}}$ (which is identical to the maximum of the $\Delta G^{\mathrm{E}}$ dependence) does not coincide with the maximum of the experimental curve, $\Delta[\eta]_{\mathrm{exp}}$. This is clearly illustrated for the system polystyrene-cyclohexane-benzene in Figure 9 showing the solvent-composition dependence of (a) experimentally determined intrinsic viscosities

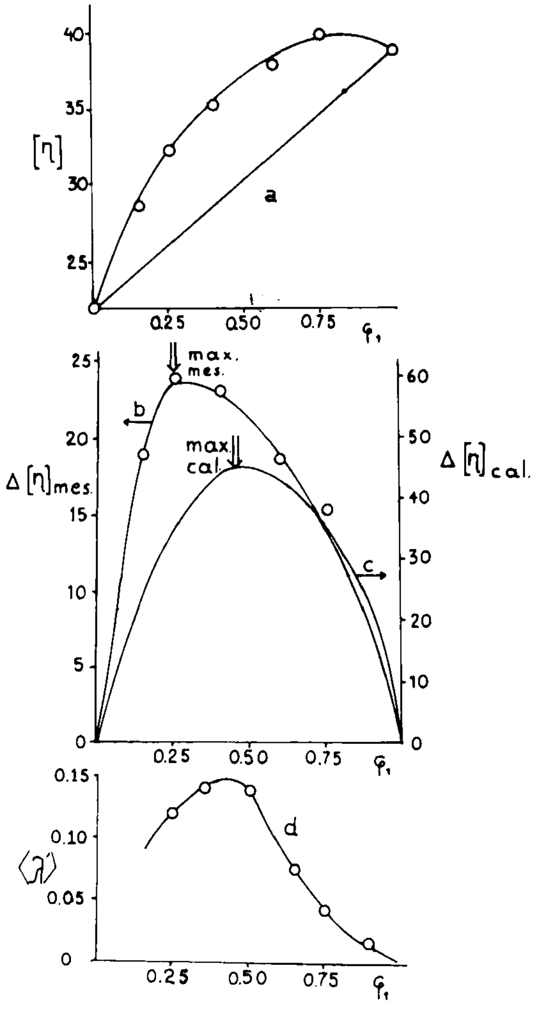

FIGURE 9 Dependence of $[\eta]$, $\Delta[\eta]_{\mathrm{exp}}$, $\Delta[\eta]_{\mathrm{cal}}$ and $\langle\lambda'\rangle$ on the volume fraction $\phi_1$ of benzene in the solvent mixture for the system polystyrene-benzene-cyclohexane at 35°C.

$[\eta]$, (b) viscosity increments $\Delta[\eta]_{\mathrm{exp}}$ computed from experimental data, (c) viscosity increments $\Delta[\eta]_{\mathrm{cal}}$ calculated from the $\Delta G^{\mathrm{E}}$ data corresponding to the analytical composition of the mixture.[33]

As can be seen from Figure 9, the maximum of $\Delta[\eta]_{\mathrm{exp}}$ is shown by the mixture containing about 25 vol % benzene whereas the calculated curve, $\Delta[\eta]_{\mathrm{cal}}$, exhibits a maximum at ≈45 vol % benzene. This discrepancy can be explained by preferential solvation of the polystyrene chain by benzene[7] which is indicated by curve *d* in Figure 9. In order to superimpose the curves $\Delta[\eta]_{\mathrm{exp}}$ and $\Delta[\eta]_{\mathrm{cal}}$, the former one has to be shifted to compositions richer in benzene; and indeed, such a displacement can be accomplished by taking into account the values of the coefficient of preferential solvation $\langle\lambda'\rangle$. In other words, when the analytical composition of the mixture is 25 vol % benzene, the local composition is richer in benzene because of the relatively large value of $\langle\lambda'\rangle$ in this region.

In conclusion we can say that the preferential solvation exerts an important influence on the dimensions of polymers dissolved in solvent mixtures.

## References

1. R. L. Scott, *J. Chem. Phys.* **17**, 268 (1949).
2. A. R. Shultz and P. J. Flory, *J. Polymer Sci.* **15**. 231 (1955).
3. A. Dondos and D. Patterson, *J. Polymer Sci.*, Part A-2 **7**, 209 (1969).
4. M. Yamamoto and J. L. White, *Macromolecules* **5**, 58 (1972).
5. R. M. Johnsen, *Chemica Scripta* **1**, 81 (1971).
6. R. H. Ewart, C. P. Roe, P. J. Debye, and J. R. MacCarttney, *J. Chem. Phys.* **14**, 687 (1946).
7. C. Strazielle and H. Benoît, *J. Chem. Phys.* **58**, 675, 678 (1961).
8. B. E. Read, *Trans. Faraday Soc.* **56**, 382 (1960).
9. J. Pouchlý and A. Živný, *J. Polymer Sci.*, Part A-2 **10**, 1481 (1972).
10. A. Dondos and H. Benoît, *Makromol. Chem.* **133**, 119 (1970).
11. Z. Tuzar and P. Kratochvîl, *Collect. Czech. Chem. Commun.* **32**, 3358 (1966).
12. J. M. G. Cowie and S. Bywater, *J. Macromol. Chem.* **1**, 581 (1966).
13. S. Brownstein, S. Bywater, and J. M. G. Cowie, *Trans. Faraday Soc.* **65**, 2480 (1969).
14. K. Sato and A. Nishioka, *J. Polymer Sci.*, Part A-2 **10**, 489 (1972).
15. E. F. Casassa and H. Eisenberg, *J. Phys. Chem.* **65**, 427 (1961).
16. K. Okita, A. Teramoto, K. Kawahara, and H. Fujita, *J. Phys. Chem.* **72**, 278 (1968).
17. P. Debye, *J. Phys. Chem.* **51**, 18 (1947).
18. A. Dondos and H. Benoît, *J. Polymer Sci.*, Part B **7**, 335 (1969).
19. P. J. Flory, *Principles of Polymer Chemistry*, Cornel University Press, Ithaca, N.Y. (1953).
20. A. Živný, J. Pouchlý, and K. Šolc, *Collect. Czech. Chem. Commun.* **32**, 2753 (1967).
21. A. Dondos and H. Benoît, *Macromolecules* **6**, 242 (1973).
22. G. François, *Ph.D. Thesis*, University of Brussels, Belgium, (1970).
23. H-G. Elias and O. Etter, *Makromol. Chem.* **66**, 56 (1963).
24. J. M. G. Cowie, *J. Polymer Sci.*, Part C **23**, 267 (1968).
25. W. H. Stockmayer and M. Fixman, *J. Polymer Sci.*, Part C **1**, 137 (1963).
26. A. Dondos and H. Benoît, *Eur. Polym. J.* **4**, 561 (1968).
27. A. Dondos and H. Benoît, *Eur. Polym. J.* **6**, 1439 (1970).
28. G. Tanaka, S. Imai, and H. Yamakawa, *J. Chem. Phys.* **52**, 2639 (1970).
29. H. Tompa, *Polymer Solutions*, Butterworths, London (1956).

30. H. Lange, *Kolloid-Z. Z. Polym.* **209/1,** 26 (1966).
31. G. M. Wilson, *J. Amer. Chem. Soc.* **86,** 127 (1964).
32. A. Dondos, K. Viras, and F. Aroni, *Eur. Polym. J.*, **9,** 1051 (1973).
33. G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Phys. Chem.* **43,** 119 (1939).

## DISCUSSION

**Dr. D. J. Meier** (*Midland Macromolecular Institute, Midland, Michigan*): In the evaluation of intrinsic viscosities in systems which show preferential solvation, is it necessary to take into account the local change in the viscosity of the medium resulting from the local change of composition?

**Prof. A. Dondos:** That possible effect has not been taken into account. Nevertheless, we shall try to analyze the problem to see if it is necessary, and, if so, the possible magnitude of the effect.

**Dr. D. J. Meier:** Is the relationship $\lambda' = \lambda_\infty' + a\rho$, which is used to determine $\langle\lambda'\rangle$, an empirical relationship or is it based on other factors?

**Prof. A. Dondos:** This relationship is considered to be semi-empirical.