

The Relationship between the Unperturbed Dimensions of Polymers in Mixed Solvents and the Thermodynamic Properties of the Solvent Mixture

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ABSTRACT: The unperturbed dimensions of polystyrene and poly(2-vinylpyridine) have been measured in solvent-precipitant mixtures of various compositions using the Stockmayer-Fixman representation. It is possible to obtain a linear relationship between K_θ and ΔG^E (the excess free enthalpy of mixing of the solvents) if, instead of using the bulk composition of the mixture, one introduces its "local" composition. This composition is calculated from the values of the preferential adsorption coefficient measured by light scattering.

In three recent papers¹⁻³ we have shown that in mixed solvents the unperturbed dimensions of macromolecules can vary considerably depending on the solvent-solvent interactions and on the polarity of the polymer. To investigate this effect more precisely, we have experimentally determined the quantity K_θ which characterizes the unperturbed dimensions and which is equal, by definition, to $[\eta]_\theta M^{-1/2}$, where $[\eta]_\theta$ is the limiting viscosity number with no excluded volume effect. If one uses Flory's theory, K_θ is related to the unperturbed end to end distance r_0^2 by the classical relation

$$K_\theta = \Phi_0 (\overline{r_0^2} / M_w)^{3/2}$$

where Φ_0 is the Flory's universal constant.

In order to obtain the K_θ values of the polymers, we have used the Stockmayer-Fixman representation⁴

$$[\eta]M^{-1/2} = K_\theta + 0.51\Phi_0 BM^{1/2}$$

which in this case should be perfectly valid, since in all of our experiments the excluded volume effect was small.

We have shown in a preceding paper³ that if one plots the quantity

$$X = K_\theta / (\varphi_1 K_{\theta_1} + \varphi_2 K_{\theta_2}) \quad (1)$$

where K_θ , K_{θ_1} , and K_{θ_2} are the values obtained in the solvent mixture, and in the pure solvents 1 and 2, respectively, as functions of the excess free enthalpy of mixing of the solvent mixture characterized by the volume fraction φ of solvent 1, one obtains a straight line. These results had been obtained for polystyrene and poly(2-vinylpyridine) in various solvent mixtures, but at constant $\varphi_1 = 1/2$. Each solvent mixture was characterized by its ΔG^E value taken from the literature.

This result was rather surprising. Therefore, we have made a number of additional experiments using other solvent mixtures over a wide range of composition in order to determine whether this behavior is general. As long as we were using two good solvents for the polymer chain, the results were in good agreement with our previous findings; but when we attempted to use mixtures of one good solvent and one precipitant for the polymer, there was absolutely no agreement. We desire to show, in the present

paper, that if one takes into account preferential adsorption, it is possible to generalize our former interpretation to the case where one component of the mixture is a non-solvent of the polymer; that is, in the case where preferential solvation can be important.

The idea according to which preferential solvation could play a role in the unperturbed dimensions of a polymer in a solvent mixture has already been tentatively expressed in another of our previous papers.⁵ It had been found that the increment ΔK_θ of unperturbed dimensions is smaller in some solvent mixtures than was expected from the value of the excess free energy of mixing of the two constituents. Since ΔK_θ is a percentage increment, it is obviously equal to $100(X - 1)$.

Experimental Section

We have used several samples of polystyrene and of poly(2-vinylpyridine), the molecular weights of which ranged from 20,000 to 500,000. These samples were prepared by anionic polymerization. Their molecular weights were determined by light scattering. They are rather monodisperse since the ratio M_w/M_n is less than 1.2 in every case as shown from the GPC diagrams. All of the solvents were distilled before use. The viscosities were measured in a classical Ubbelohde viscometer at constant pressure and at 25°.

In order to obtain K_θ for a given solvent composition we have plotted $[\eta]M^{-1/2}$ as function of $M^{1/2}$, $[\eta]$ being the limiting viscosity number of the sample of molecular weight, M .

In some cases the points corresponding to low molecular weights deviate slightly from the straight line. This can be explained by the variation of preferential adsorption when the molecular weight diminishes near the precipitation point.⁶ In order to eliminate this effect we did not take these points into account.

Since we wished to know precisely, for each composition, the amount of preferential solvation of one of the constituents of the mixture, we have also carried out light-scattering experiments at the same solvent composition and at the same temperature. This allows one to measure an apparent molecular weight and to calculate from it, according to a well-known procedure,⁷ the coefficient λ' , related to preferential adsorption by

$$\lambda' = (\gamma_1/M)V_1$$

where γ_1 is the number of molecules of type 1 and molar volume V_1 adsorbed preferentially in the vicinity of the macromolecular chain. The results are collected in the four first columns of Tables I-V. The caption of these tables gives information on the polymers and on the solvent precipitant mixtures used. In Figures 1-5, we have plotted K_θ and λ' as functions of solvent composition. Very different behaviors can be observed depending on the type of solvent mixture. When λ' increases rapidly, on addition of a precipitant, there is a marked diminution of K_θ near the precipitation point (Figures 1 and 5). On the contrary, if λ' does not vary appreciably

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(1) A. Dondos and H. Benoit, *Eur. Polym. J.*, **4**, 561 (1968).

(2) A. Dondos and H. Benoit, *Eur. Polym. J.*, **6**, 1439 (1970).

(3) A. Dondos and H. Benoit, *Macromolecules*, **4**, 279 (1971).

(4) W. H. Stockmayer and M. Fixman, *J. Polym. Sci., Part C*, **1**, 137 (1963).

(5) A. Dondos, P. Rempp, and H. Benoit, *J. Polym. Sci., Part C*, **30**, 9 (1970).

(6) A. Dondos and H. Benoit, *Makromol. Chem.*, **133**, 119 (1970).

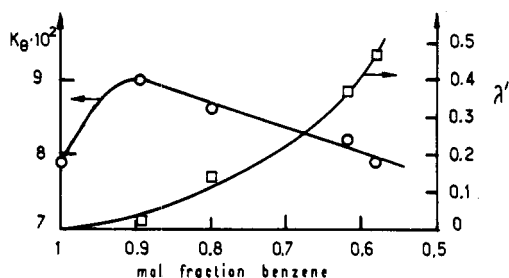


Figure 1. Variation of K_{Θ} and λ' for polystyrene solutions in benzene-methanol mixture as a function of the bulk molar composition of the mixture.

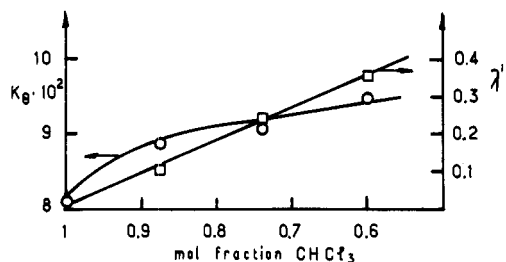


Figure 2. Variation of K_{Θ} and λ' for polystyrene solutions in CHCl_3 -ethanol mixture as a function of the bulk molar composition of the mixture.

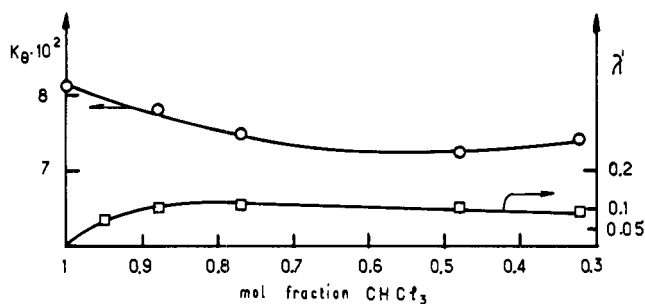


Figure 3. Variation of K_{Θ} and λ' for polystyrene solutions in CHCl_3 -acetone mixture as a function of the bulk molar composition of the mixture.

ciably with the composition of the solvent mixture K_{Θ} either increases or stays constant (Figures 2 and 3).

Results

In order to explain these results, we shall assume that preferential adsorption affects mainly the solvent molecules which are in the immediate neighborhood of the macromolecular chain. This assumption seems to be valid as long as the phenomenon of preferential adsorption does not depend on molecular weight. Since for the calculation of K_{Θ} we did not take into account the lowest molecular weight samples for which there could be an effect of the internal concentration⁶ this model seems to be quite appropriate. Owing to this preferential adsorption the solvent composition is quite different in the vicinity of the macromolecules from what it is at a long distance from it. Since unperturbed dimensions are only sensitive to local conformation and therefore to the local composition of the solvent mixture, it seems to be more reasonable to compare this parameter ΔK_{Θ} with the ΔG^E value corresponding to the actual local composition, near to the chain backbone, rather than to its bulk (or analytical) composition.

This "local" composition cannot be evaluated without making an assumption about the number of immediate neighbor solvent molecules per monomeric unit. In the following we shall characterize this number by the param-

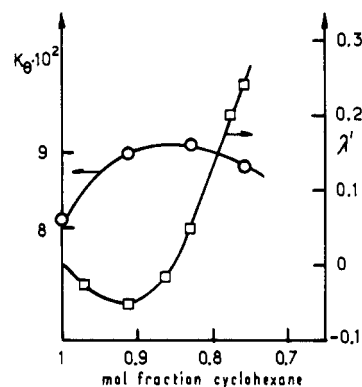


Figure 4. Variation of K_{Θ} and λ' for polystyrene solutions in cyclohexane-ethanol mixture as a function of the bulk molar composition of the mixture.

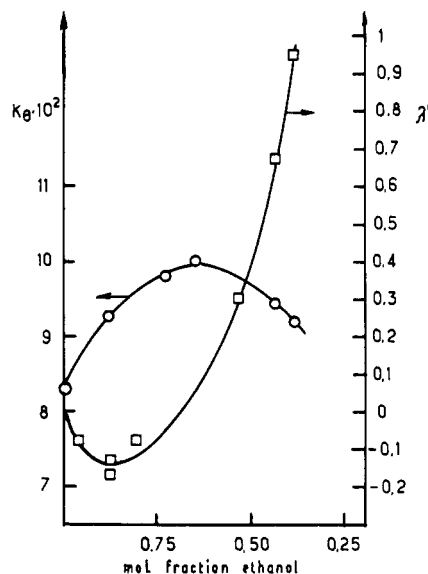


Figure 5. Variation of K_{Θ} and λ' for poly(2-vinylpyridine) solutions in ethanol-cyclohexane mixture as a function of the bulk molar composition of the mixture.

eter Z . If we assume that the number of monomeric units of the chain is N , there will be NZ sites available for adsorption.

If the adsorbed solvent had the same molar composition as the bulk of the solvent mixture we would have respectively NZx_1 and NZx_2 molecules of solvent 1 and 2 on these sites. The quantity x_1 is the molar fraction of constituent 1 in the mixture.

The definition of the coefficient of preferential adsorption λ' tells us that we have γ_1 molecules of species 1 added in the vicinity of the coil and that $\lambda\gamma_2$ molecules of species 2 have been removed, γ_1 and γ_2 being calculated from the relationship⁷

$$\gamma_1 V_1 = \gamma_2 V_2 = \lambda' M = \lambda' m N$$

where m is the molar mass of the monomeric unit and V_1 and V_2 the molar volumes of the two solvents. Accordingly, the corrected number of molecules of species 1 and 2 along the chain will be

$$\begin{aligned} NZx_1 + \gamma_1 \\ NZx_2 - \gamma_2 \end{aligned}$$

(7) C. Strazielle and H. Benoit, *J. Chim. Phys.*, **38**, 675, 678 (1961).

Table I
System Polystyrene-Benzene-Methanol

| x_1 | $K_\theta \times 10^2$ | ΔK_θ (%) | λ' | x_1' | ΔG^E ^a (cal mol ⁻¹) |
|-------|------------------------|-----------------------|------------|--------|--|
| 1 | 7.9 | | | 1 | |
| 0.895 | 9.0 | 12.6 | ~0 | 0.895 | 115 |
| 0.80 | 8.6 | 8.8 | 0.14 | 0.915 | 95 |
| 0.62 | 8.25 | 4.4 | 0.37 | 0.930 | 80 |
| 0.58 | 7.9 | 0 | 0.47 | 0.963 | 45 |

^a G. M. Wilson, *J. Amer. Chem. Soc.*, **86**, 127 (1964).

Table II
System Polystyrene-CHCl₃-Ethanol

| x_1 | $K_\theta \times 10^2$ | ΔK_θ (%) | λ' | x_1' | ΔG^E ^a (cal mol ⁻¹) |
|-------|------------------------|-----------------------|------------|--------|--|
| 1 | 8.1 | | | 1 | |
| 0.875 | 8.9 | 9.9 | 0.1 | 0.932 | 65 |
| 0.74 | 9.1 | 12.3 | 0.238 | 0.882 | 95 |
| 0.60 | 9.5 | 17.3 | 0.365 | 0.810 | 135 |

^a G. Scatchard and G. L. Raymond, *J. Amer. Chem. Soc.*, **60**, 1278 (1938).

Table III
System Polystyrene-CHCl₃-Acetone

| x_1 | $K_\theta \times 10^2$ | ΔK_θ (%) | λ' | x_1' | ΔG^E ^a (cal mol ⁻¹) |
|-------|------------------------|-----------------------|------------|--------|--|
| 1 | 8.1 | | | 1 | |
| 0.880 | 7.75 | -4.3 | 0.100 | 0.927 | -60 |
| 0.767 | 7.5 | -7.4 | 0.102 | 0.815 | -110 |
| 0.480 | 7.25 | -10.4 | 0.100 | 0.530 | -150 |
| 0.320 | 7.4 | -8.6 | 0.090 | 0.360 | -130 |

^a J. A. Barker and F. Smith, *J. Chem. Phys. Soc.*, **22**, 375 (1954).

Table IV
System Polystyrene-Cyclohexane-Ethanol

| x_1 | $K_\theta \times 10^2$ | ΔK_θ (%) | λ' | x_1' | ΔG^E ^a (cal mol ⁻¹) |
|-------|------------------------|-----------------------|------------|--------|--|
| 1 | 8.1 | | | 1 | |
| 0.917 | 9.0 | 11 | -0.05 | 0.87 | 180 |
| 0.830 | 9.1 | 12.3 | +0.05 | 0.86 | 190 |
| 0.760 | 8.8 | 8.6 | +0.24 | 0.90 | 150 |

^a See footnote to Table I.

Table V
System Poly(2-vinylpyridine)-Ethanol-Cyclohexane

| x_1 | $K_\theta \times 10^2$ | ΔK_θ (%) | λ' | x_1' | ΔG^E ^a (cal mol ⁻¹) |
|-------|------------------------|-----------------------|------------|--------|--|
| 1 | 8.30 | | | 1 | |
| 0.88 | 9.25 | 14.2 | -0.15 | 0.83 | 180 |
| 0.73 | 9.80 | 24.0 | 0 | 0.73 | 250 |
| 0.65 | 10.00 | 28.5 | 0 | 0.65 | 290 |
| 0.44 | 9.45 | 26.0 | 0.67 | 0.71 | 260 |
| 0.39 | 9.20 | 23.5 | 0.95 | 0.76 | 230 |

^a See footnote to Table I.

If we now assume that the molar volumes V_1 and V_2 are sufficiently close together in order to allow the same value of Z to be valid for both solvents surrounding the chain, the actual molar fraction x_1' of solvent 1 along the chain is given by

$$x_1' = [Zx_1 + \lambda'(m/V_1)] / [Z + \lambda'[(m/V_1) - (m/V_2)]]$$

It should be emphasized that the value of x_1' is very sensitive to the choice of the value of the parameter Z . If Z is

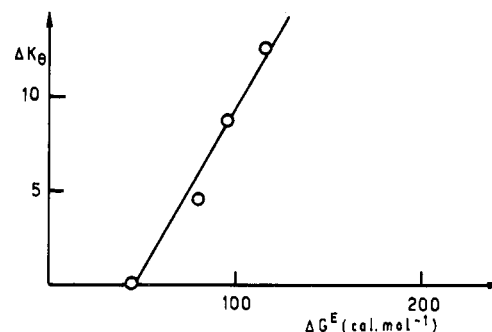


Figure 6. Relationship between the increment of K_θ and ΔG^E ("local") for the system polystyrene-benzene-methanol.

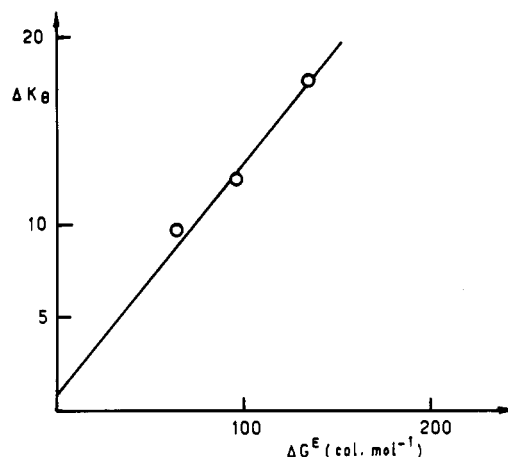


Figure 7. Relationship between the increment of K_θ and ΔG^E ("local") for the system polystyrene-CHCl₃-ethanol.

too large, x_1' approaches x_1 ; if Z is too small, one could obtain values of x_1' larger than 1 which is, of course, meaningless. The choice of a correct value of Z is therefore very important. In this paper, we have adopted for Z the value 3. This value is reasonable according to Tompa.⁸ In the fifth column of Tables I-V, the values of the molar composition of the solvent mixture, in the vicinity of the molecules, are evaluated by this method.

One sees that the values of x_1' are quite different from the bulk molar composition. In the last column we have collected the ΔG^E values corresponding to the "local" composition of the solvent as they can be found in literature.

Discussion

Despite the crudeness of the approximation we have made for evaluating the local concentration, the treatment affords, in our opinion, some clarification in the interpretation of the variation of unperturbed polymer dimensions as a function of the amount of added precipitant. It is clearly established that the differences observed are due mainly to differences in λ' . In order to show this we have drawn in Figures 6, 7, 8, and 9 the increments ΔK_θ as functions of ΔG^E , the excess free enthalpy of mixing of the solvents corresponding to the "local" composition of the mixture along the chain. The linearity of the obtained plots is quite satisfactory.

For polystyrene ΔK_θ represents the difference (in percent) between the value for the good solvent and the actual value. For poly(2-vinylpyridine) we take into consideration two values of K_θ : the value in pure ethanol and a

(8) H. Tompa, "Polymer Solutions," Butterworths, London, 1956.

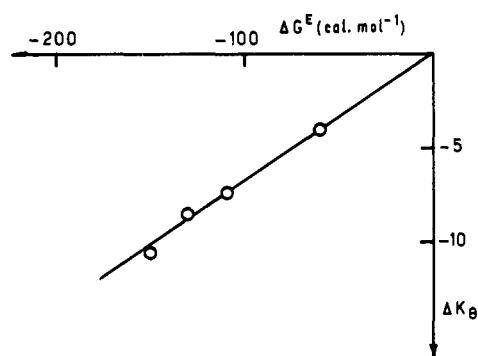


Figure 8. Relationship between the increment of K_Θ and ΔG^E ("local") for the system polystyrene- CHCl_3 -acetone.

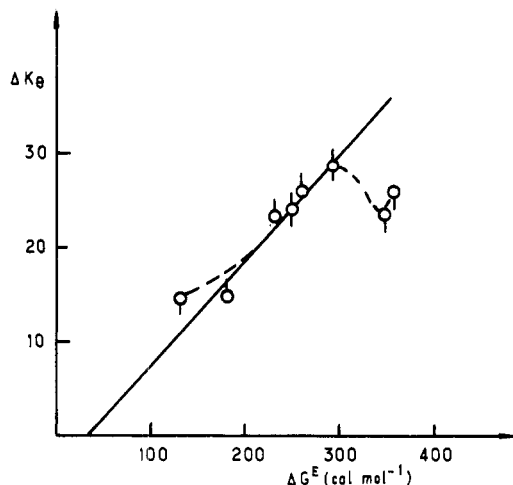


Figure 9. Relationship between the increment of K_Θ and ΔG^E for the system poly(2-vinylpyridine)-ethanol-cyclohexane. (○) ΔG^E values corresponding to the analytical (bulk) molar composition of the mixture. (●) ΔG^E values corresponding to the "local" molar composition of the mixture, along the chain.

second value valid for nonpolar solvents in which no association phenomena occur.⁹

Even if one questions the exact value of the Z parameter, it is very striking to see that plots of ΔK_Θ as a function of the bulk solvent composition yield curves of very different shapes, but if one uses our representation one obtains almost straight lines.

Our calculations explain for instance why at the precipitation point ΔK_Θ is practically zero for the system poly-

styrene-benzene-methanol and very large for the system polystyrene-chloroform-ethanol. In the first case there is a strong adsorption of benzene which practically maintains the coil in pure benzene (from our calculation we have $x_1' = 0.963$), in the second case there is much less preferential solvation, therefore the "local" and the bulk compositions are more similar.

Another example of this type of behavior is given by the system polystyrene-carbon tetrachloride-methanol. From our measurements it follows that the K_Θ value obtained is practically the same in pure CCl_4 and near the precipitation of the polymer, at a composition of the mixture which behaves like a Θ solvent (molar fraction of CCl_4 $x_1 = 0.65$).⁶ Taking into account the value λ' ,⁶ one finds x_1' to be of the order of one, showing again that the same value of K_Θ is obtained only for identical compositions of the solvent mixture in the vicinity of the coil.

Another interesting point concerns the cases of poly(2-vinylpyridine) in ethanol-cyclohexane mixtures and of polystyrene in cyclohexane-ethanol mixtures. As in some other cases, an inversion of selective adsorption¹⁰⁻¹⁴ takes place: at low concentrations of precipitant (cyclohexane for poly(2-vinylpyridine) and ethanol for polystyrene) it turns out that the precipitant is preferentially adsorbed, while at high concentration of precipitant the good solvent is adsorbed. This anomalous behavior has no influence on K_Θ if one uses our representation, i.e., K_Θ as function of the ΔG^E value corresponding to the "local" concentration. If one uses the bulk composition of the mixture, one obtains the dotted line of Figure 9.

All of the results show that it is much easier to obtain an interpretation of the local conformation of polymer molecules characterized by their unperturbed dimensions, if instead of using the bulk composition of the solvent mixture, one corrects this value by taking into account the local changes of composition due to preferential adsorption. Another fact which seems to be important is the relationship between K_Θ and the interactions of the solvents, characterized by ΔG^E . At first sight these two quantities seem to be quite independent, one characterizes the polymer conformation and the other the solvent mixture. The present results show that this relation rests on a sound experimental basis.

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(10) J. Pouchly, A. Zivny, and K. Solc, *J. Polym. Sci., Part C*, **23**, 245 (1968).

(11) Z. Tuzar and H. C. Beachell, *Polym. Lett.*, **9**, 37 (1971).

(12) A. Dondos, *C. R. Acad. Sci., Ser. C*, **272**, 1419 (1971).

(13) J. M. G. Cowie, R. Dey, and J. T. McCrindle, *Polym. J.*, **2**, 88 (1971).

(14) S. Sato and A. Nishioka, *Polym. J.*, **3**, 244 (1972).