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The concentration fluctuations in polymer–mixed solvent systems

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A study of the ternary polymer systems dimethyl formamide–ethyl acetate–PS, chloroform–1,4 dioxane–PS and cyclohexane–benzene–PS was carried out by classical light scattering. Through the concept of a complex between polymer and sorbed solvent a qualitative agreement has been found between the composition light scattering and the total sorption. For the system cyclohexane–benzene–PS, it was shown that a strong and specific interaction between polymer and nonpreferentially adsorbed solvent can overcompensate the effect of the binary solvent interaction parameter χ_{12}. It seems, that not only the intrinsic viscosity and the coil radius of gyration but also the concentration fluctuations (or fluctuations in the structure of the polymer complex) may serve as a description of the linear expansion of the polymer coil. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Polymers in mixed solvents form different systems interesting from the theoretical as well as practical point of view. Equilibrium and transport properties of ternary polymer solutions (TPS) have been widely used to describe binary and ternary interactions between the components of the TPS systems. Since a useful information about the interactions in such systems may also be given by the method of light scattering (LS)[1,2], the aim of this paper is the study of basic LS quantities in the solutions of polystyrene (PS) in the binary solvents 1,4-dioxane (D)–chloroform (C), cyclohexane (H)–benzene (B) and dimethylformamide (DMF)–ethyl acetate (EA). The selection of these pairs of solvents was influenced by the fact that the binary solvent EA–DMF is a cosolvent[3], D–C a cononsolvent[3] and the behaviour of the mixture H–B–PS is influenced by the association of cyclohexane molecules[4].

THEORY

For the understanding of phenomena observed in an ensemble of macromolecules dissolved in a mixed solvent, the effect of the preferential or the total sorption is of prime importance. By the last effect the equilibrium is characterized by the total amount of mixed solvent sorbed in the polymer region and is described by the linear expansion of the macromolecular coil. Pouchlý and Živný[5] have shown that the total sorption equilibrium can be represented by the osmotic pressure or by the second virial coefficient of the osmotic pressure, A_2, of the polymer solution and the dependence of these quantities on the composition of mixed solvent can exhibit maxima and minima. According to Kratochvíl[2] the LS behaviour of TPS can often be explained by introducing the concept of a complex formed by the polymer and sorbed solvent. Then the entities responsible for the intensity of LS from a dilute solution of a polymer in a mixed solvent are the particles of this complex—the complex molecules, and not the polymer molecules themselves. The well known basic equation, describing the scattering from concentration fluctuations in a polymer solution, $R^{c}(\theta)$, can be written in terms of the complex in the form

$$R_{u}^{c^*}(\theta) = R_{u}(\theta)_{\text{solutions}} - R_{u}(\theta)_{\text{solvent}} = \frac{K'(\mathrm{d}n/\mathrm{d}c^*)^2 c}{[1/M^* P^*(\theta)] + 2A_2^* + \cdots} \qquad (1)$$

where R_u is the Rayleigh ratio in an unpolarized primary beam, K' is the optical constant, θ is the angle of observation and the asterisk denotes parameters of the complex. According to this relation a close relationship between $R^{c^*}(\theta)$ and A_2^* exists; then, by estimating concentration dependences of $R^{c^*}(\theta)$ it is possible to obtain information on thermodynamic behaviour of polymer–mixed solvent solutions. M^*, A_2^* and $P^*(\theta)$ has no physical meaning in itself, they are a function of the real M_w, A_2, $P(\theta)$ and the coefficient of the selective sorption. As the variations of the second virial coefficient with solvent composition at constant M were discussed further, the differences between A_2^* and A_2 were not crucial.

For the characterization of the interaction occurring in binary solvent alone, we can start with relation[6]

$$R_{u}^{\text{tot}}(\theta) = R_{u}^{\text{is}}(\theta) + R_{u}^{\text{an}}(\theta) \qquad (2)$$

where R_u is the Rayleigh ratio for total, isotropic and anisotropic LS. Here $R_{u}^{\text{an}}(\theta)$ reflects translational–orientational fluctuations of anisotropically polarizable

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molecules and the isotropic scattering by a mixture may be regarded as a sum of fluctuations in density and concentration

$$R_u^{is}(\theta) = R_u^{d}(\theta) + R_u^{c}(\theta) \qquad (3)$$

The scattering parameters R_u^{is}, R_u^{an} can be calculated on the basis of experimental determination of R_u^{tot} and depolarization $D_u = H_u/V_u$ (H_u, V_u are Rayleigh's ratios for the horizontally and vertically polarized components of the scattered light at $\theta = 90°$) and using the well-known equations

$$R_u^{is} = R_u^{tot}(6 - 7D_u)/(6 + 6D_u) \qquad (4)$$

$$R_u^{an} = R_u^{tot}(13D_u)/(6 + 6D_u) \qquad (5)$$

Hereby for D_u it holds primarily[7]

$$D_u = \frac{(6/13)R_u^{an}}{R_u^{is} + (7/13)R_u^{an}} \qquad (6)$$

and so by estimating concentration dependences of R_u^{is}, R_u^{an} and D_u it is possible to obtain information on the structure or intermolecular interactions in a mixed solvent.

EXPERIMENTAL

The solvents were purified by two-fold distillation. The solvent solution of different composition were prepared by pipetting directly into measuring cells in a dust-free medium.

Standard PS was from the Rubber and Plastics Research Association of Great Britain, Shawbury ($M_w = 310\,000\,\mathrm{g\,mol^{-1}}$). Its solutions were prepared by weighing and dissolving PS in individual components of binary solvent and these solutions were mixed up in required volumes. The dust particles were removed by pressure filtration through a porous glass filter G5 (Schott, Jena).

The light scattering was measured with a photogoniodiffusionmeter 'Sofica' at the wavelength of 546 nm at 23°C. Benzene was used as a standard for the calculation of individual scattering quantities ($R_u^{tot} = 16.2 \times 10^{-6}\,\mathrm{cm^{-1}}$). The error of R_u^{tot} determinations was always lower than 5%, for D_u lower than 8%.

RESULTS AND DISCUSSION

Before discussing the results obtained from LS data, let us observe *Figure 1* illustrating the course of A_2 as a function of solvent composition in typical TPS[3]. The cosolvent system DMF–EA–PS shows a maximum, while the opposite case is shown by the D–C–PS mixture. The solvent composition corresponding to the maximum of A_2 is the one which is the thermodynamically most powerful solvent for polymer and vice versa.

As the coefficient A_2^* is connected with composition LS through the relation (1), it is interesting to compare *Figure 1* with *Figure 2*, where the dependence $\Delta R_u^{c^*}(90)$ on composition of mixed solvent is depicted. Here $\Delta R_u^{c^*}(90)$ means difference between $R_u^{c^*}$ for the polymer complex in the solvent mixture and a 'theoretical average' at the same solvent composition which lies on the straight line joining the values of $R_u^{c^*}$ in the pure solvents

$$\%\Delta R_u^{c^*}(90) = \frac{R_u^{c^*}(90) - R_u^{c^*}(90)_{ideal}}{R_u^{c^*}(90)_{ideal}} \times 100 \qquad (7)$$

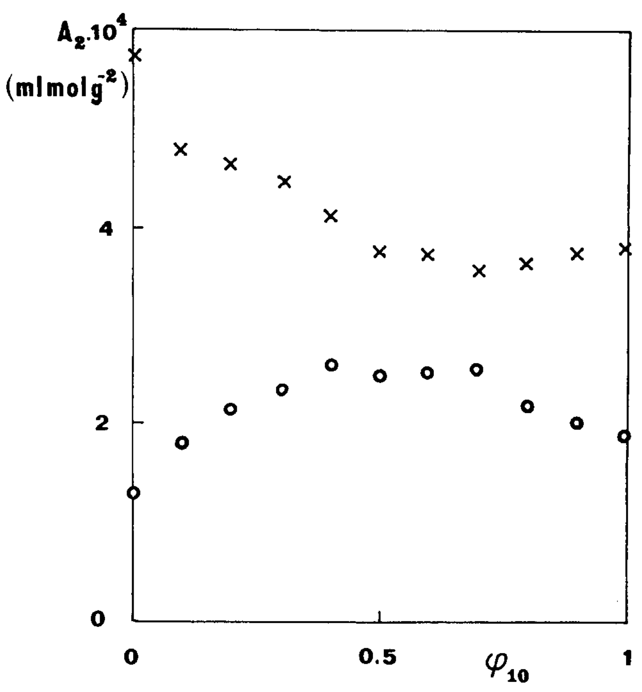

Figure 1 Dependence of the real second virial coefficient for the sample PS 384 with the solvent composition, for the systems DMF–EA (○) and D–C (×) [3]; φ_{10} is the volume fraction of DMF or D

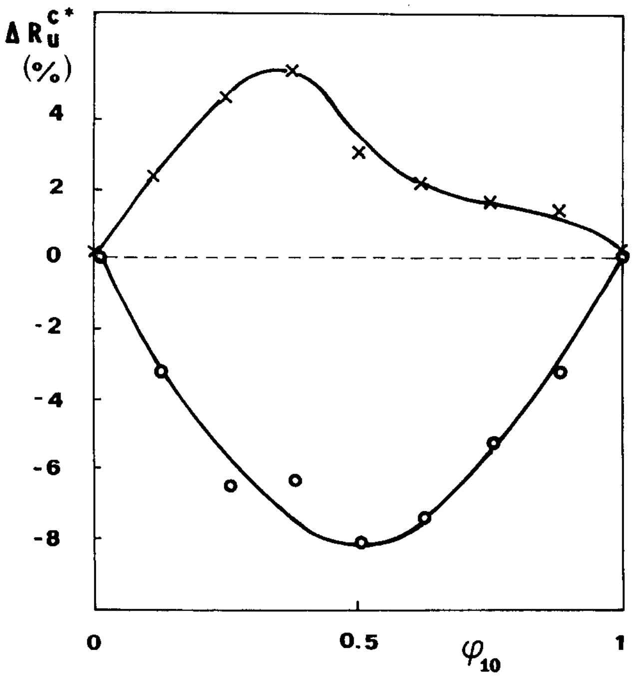

Figure 2 The course of the concentration fluctuations for standard PS in the binary solvents DMF–EA (○) and D–C (×); concentration of PS was 1.5 mg cm^{-3}

Already, by a qualitative comparison of *Figure 2*, we can see that theoretical predictions are completely fulfilled by the ascending values of A_2 polymer molecules preferring contacts with solvent molecules, the solvation

Table 1 Physical chemical parameters of mixed solvents components[7]

Solvent	Solubility parameter (Hildebrand)	Fractional polarity p	Hydrogen-bonding θ_H
Dioxan	10.0	0.006	14.6
Chloroform	9.0	0.017	1.5
Ethyl acetate	9.1	0.167	8.4
Dimethylformamide	12.1	0.772	18.9

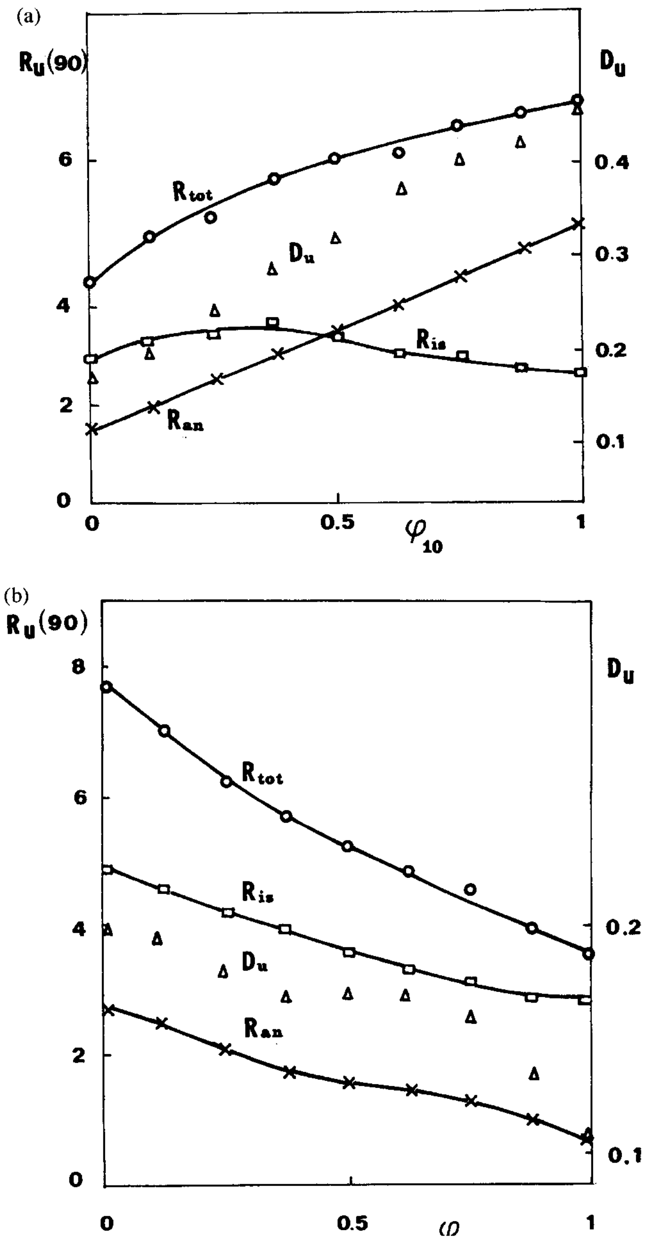

Figure 3 Concentration dependences of the basic light-scattering quantities R_u^{tot}, R_u^{is}, R_u^{an} (10^{-6} cm^{-1}) and D_u in the mixed solvent: (a) DMF–EA, (b) D–C

reducing the free volume available for concentration fluctuation and in this sense the values of $R_u^{c^*}$ should be diminishing. On the contrary, at the descending values of A_2 the probability of concentration fluctuations increases and in this way the values of $R_u^{c^*}$ increase too. So it seems, that instead of A_2 the quantity $R_u^{c^*}$ can be used by thermodynamics of TPS and that not only the intrinsic viscosity and the coil radius of gyration but also the composition LS may serve as a description of the linear expansion of the polymer coil.

As the preferential or total sorption is influenced by the nature of the solvents, we further focus our attention on this problem.

To obtain reliable predictions of polymer solubility behaviour, various workers have attempted to correlate experimental data with intermolecular forces[7]. Nelson *et al.* use Hildebrand's solubility parameter δ, fractional polarity p and hydrogen bonding index θ_H; here p is the polar fraction of the total potential energy of the substance and θ_H reflects the ability of a molecule to form a hydrogen-bond. The δ, p and θ_H values for solvents under consideration are listed in *Table 1*. From inspection of *Table 1* and *Figure 2* we can judge mainly that the addition of a solvent with lower value of p tends to cononsolvency and the effect of cosolvency is caused by addition of a solvent with higher polarity; in our case DMF will dispel both EA and PS, thus favouring the adsorption of EA on the polymer (EA has less affinity to PS than DMF). Here a similar mechanism of interactions was proposed in the system PS–B–isopropanol by Cowie and Bywater[8]. In the mixture C–D, cononsolvency may be attributed, moreover, to large differences in θ_H values. These statements are in correlation with the results of the LS study of binary solvents C–D and EA–DMF (*Figure 3*). One can observe that already the course of the basic LS characteristic show differences in the molecular interactions in the considered mixtures. Let us follow the concentration dependence of D_u; D_u has a crucial importance in computing R_u^{is} or R_u^{an} and it serves as an important structural optical constant[6,9]. D_u in the case of C–D mixture manifests a positive deviation from linearity, whereby the linearity is typical for solutions without associates and complexes[9]. From this nonlinear course of D_u, together with a similar course of R^{an} and a little negative deviation of R^{is} from linear character, it is possible to conclude that in the mixture D–C the ability of these solvents to associate exists. Then, these interactions between pairs of molecules D–C show, that in the mixture D–C–PS, affinities D–PS and C–PS are weakened and cononsolvency is present. Similar examples have already been given by Gee[10] who showed that cellulose acetate, soluble in formic acid and aniline, is nonsoluble in a mixture of these solvents. Here, strong acidobasic interactions between molecules of binary solvent prevail with interactions between polymers and arbitrary individual solvents.

The third system under study was PS–B–H where the binary solvent has a positive value of χ_{12} (χ_{12} is the binary solvent interaction parameter) and so by the dependence of the total sorption (expressed through A_2) on the composition of the mixed solvent a maximum can be expected[5] and thus by R^{c^*} a minimum. The course of composition LS in this system is depicted in *Figure 4*; as can be seen, the concentration fluctuations, contrary to expectations, are present in a high degree and thus optical microheterogeneity is appreciable here. About the system B–H–PS is known the sorption of B on PS is little because association between molecules of H exists[4]. In this case a maximum on the dependence A_2–binary solvent composition does not exist and $A_2 = 4.1 \times 10^{-4}$ (ml g^{-2} mol^{-1}) in pure B is falling to $A_2 = 1.5 \times 10^{-4}$ in the mixture B/H = 1/3[4]. It is evident that the solvent mixture becomes worse as the amount of H increases and strong specific interaction between H

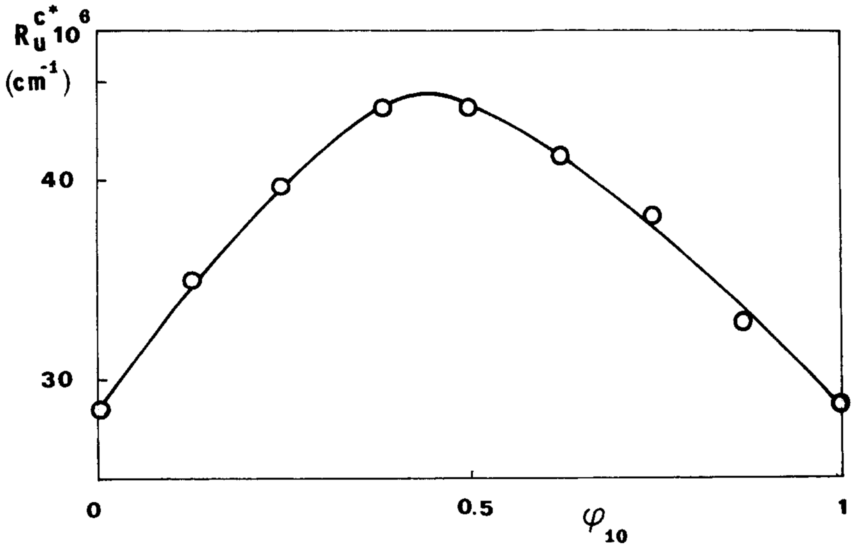

Figure 4 Composition light-scattering in the system PS–B–H; φ_{10} is the volume fraction of B, concentration of PS was 1.5 mg cm^{-3}

and the polymer molecule is to be expected. In this connection Lange[11] showed that in mixtures of B with paraffins the PS adsorption of a paraffin with molecules of cyclical shape (cyclohexane) is stronger than the adsorption of a paraffin with molecules of equal size but linear (*n*-hexane). Simultaneously, he showed that the number of molecules adsorbed on PS for individual components of the binary solvent H–B with the increasing presence of H(B) is rising practically linearly within the whole concentration interval and by $\varphi_H \doteq 0.55$ on PS an equal number of molecules H and B are present. By this binary solvent composition the mixture PS–B–H has evidently a maximum microheterogeneity and just in this region (*Figure 4*) the concentration fluctuations (or fluctuations in the structure of the polymer–solvent complex) exhibit a maximum also. As can be expected, with the increasing amount of B or H (from concentration region $\varphi_H \doteq 0.55$) these fluctuations are decreasing.

In this connection we would like to bring into consideration the concluding remarks published in ref. 5: 'while total sorption, at a low preferential sorption and at a large positive value of χ_{12} can exhibit a maximum, a larger preferential sorption can overcompensate the effect of the parameter χ_{12} so that a minimum appears'. On the basis of our LS results and results obtained by Lange[11] for the H–B–PS system it is possible to conclude that also a strong and specific interaction between polymer and nonpreferentially adsorbed solvent can overcompensate the effect of the parameter χ_{12}.

From the standpoint of the concepts and facts presented and discussed above it is interesting to mention the results of a similar study on the PVC–DMF–tetrahydrofuran (THF) mixture already published[10]. Here the course of the dependence $R_u^{c^*}$–mixed solvent composition is passing through a pronounced minimum situated just in the region where the solubility of PVC has a maximum. PVC has hydrogen atoms which may be of sufficient activity to form hydrogen bonds. On the other hand THF and DMF are solvents with a high electron–donor capacity and so we obtain a homogeneous system, in which the fluctuations in concentration are minimum.

Finally it is possible to say that the local fluctuation of the concentration indicated by classical LS can afford information which is useful in understanding mixing from a molecular point of view.

REFERENCES

1. Strazielle, C., in *Light Scattering from Polymer Solutions*, ed. M. B. Huglin. Academic Press, London, New York, 1972, p. 633.
2. Kratochvíl, P., *Classical Light Scattering from Polymer Solutions*. Elsevier, Amsterdam, Oxford, New York, Tokyo, 1987, p. 145.
3. Gómez, C. M., Soria, V. and Campos, A., *Colloid Polymer Sci.*, 1992, **270,** 197.
4. Strazielle, C. and Benoit, H., *J. Chim. Phys.*, 1961, **58,** 675, 678.
5. Pouchlý, J. and Živný, A., *J. Polymer Sci. Part A-2*, 1992, **10,** 1481.
6. Kerker, M., *The Scattering of Light and Other Electromagnetic Radiation*. Academic Press, New York, 1969, p. 504.
7. Kumar, R. and Prausnitz, J. M., in *Solutions and Solubilities*, Part I, ed. M. R. J. Dack. Wiley, New York, 1975, p. 259.
8. Cowie, J. M. G. and Bywater, S., *J. Macromol. Chem.*, 1966, **1,** 581.
9. Vavra, J., *Colloid Polymer Sci.*, 1993, **271,** 480.
10. Gee, G., *Trans. Faraday Soc.*, 1944, **40,** 468.
11. Lange, H., *Kolloid Z.u.Z. Polymere*, 1964, **199,** 128.