

Light scattering in acetone—chloroform and acetone—chloroform—poly(methyl methacrylate) mixtures

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Dedicated to Professor E. Treindl, DrSc., in honour of his 60th birthday

The dependence of the principal characteristics of light scattering on composition of the acetone—chloroform and acetone—chloroform—poly(methyl methacrylate) mixtures was investigated. The discontinuous course of these relationships in the presence of polymer indicates the existence of a conformational transition at which the mixture exhibits disorder characterized by an increase of fluctuations in concentration and thus by an increase in isotropic as well as total light scattering.

A useful information about interactions in solutions of low- and high-molecular substances may be also supplied by the method of light scattering in connection with the study of fluctuations in density ρ , concentration c , and anisotropy. As known [1], the total light scattering (sum of isotropic and anisotropic scattering) may be expressed on the basis of contributions of the mentioned fluctuations in the following form

$$R_u^{\text{tot}} = R_u^{\text{is}} + R_u^{\text{anis}} = R_u^e + R_u^c + R_u^{\text{anis}}$$

where R_u is the Rayleigh ratio for the nonpolarized primary ray. Because of a sufficiently large volume of liquid, the local fluctuations of these three types obey the laws determined by intermolecular interactions. Therefore the study of the scattering equilibrium fluctuations depending on composition of solution (the so-called isotherms of scattering) can elucidate the laws valid for internal structure of solutions.

The topic of this paper, which follows paper [2] dealing with the PVC—THF—DMF system, is the study of R_u^{tot} , R_u^{is} , and R_u^{anis} in the acetone—chloroform and acetone—chloroform—poly(methyl methacrylate) (PMMA) mixtures.

Experimental

The purification of solvents, the preparation of solutions and the measurements of refractive index and light scattering were performed by the methods described earlier [2].

The standard PMMA ($\bar{M}_w = 170\,000 \text{ g mol}^{-1}$) was obtained from the Polymer Institute of the Slovak Academy of Sciences. The measurements were carried out at 25°C.

Results and discussion

The parameters of scattering R_u^{is} and R_u^{anis} were calculated from the experimental determination of total scattering R_u^{tot} and depolarization $D_u = H_u/V_u$ (H_u and V_u are the Rayleigh ratios of the horizontal and vertical polarized component of scattered light) by using the following equations [1, 2]

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

$$R_u^{\text{anis}} = R_u^{\text{tot}} 13D_u/(6 + 6D_u)$$

Fig. 1 represents the dependence of these quantities on composition of the acetone—chloroform mixture. First of all, let us pay attention to the course of R_u^{is} which, according to the fluctuation theory of light scattering, indicates the maximum increase in fluctuations of composition for a mixture with equal content of its components. Of course, this fact is not surprising because we know other mixtures (*e.g.* benzene—methanol [1]) with analogous properties, only the height of maximum is varying.

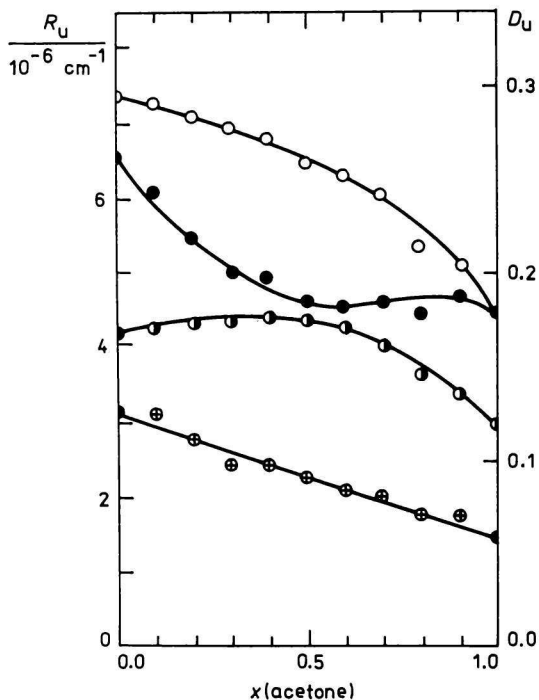


Fig. 1. Variation of scattering quantities R_u^{tot} (○), R_u^{is} (●), R_u^{anis} (⊕) and D_u (●) with composition for the acetone—chloroform mixture, R_u was measured at the observing angle 90°.

In this connection it appears that the so-called index of hydrogen bond Θ [3] could be a convenient indicator. (Θ expresses the ability of forming hydrogen bond.) Then we may state on the basis of the values of this index for components of the mixtures under consideration that the benzene—methanol mixture (Table 1) exhibits the maximum difference in the value of Θ , which manifests itself by a significant maximum on the plot of R_u^{is} vs. composition [1]. On the other hand, only a slight deviation from the linear course of isotropic scattering [2] was observed for the THF—DMF mixture. Thus the acetone—chloroform mixture occurs in the middle of these mixtures.

Table 1

Values of the hydrogen bond index Θ

Solvent	Benzene	Methanol	DMF	THF	Acetone	Chloroform
Θ	0	-19.8	18.9	12	12.5	1.5

Let us consider the influence of PMMA on individual isotherms of light scattering in accordance with Fig. 2. In agreement with the results presented in papers [4] and [2], the expected polymer—solvent interactions do not influence the anisotropic scattering within the range of experimental errors. However, the

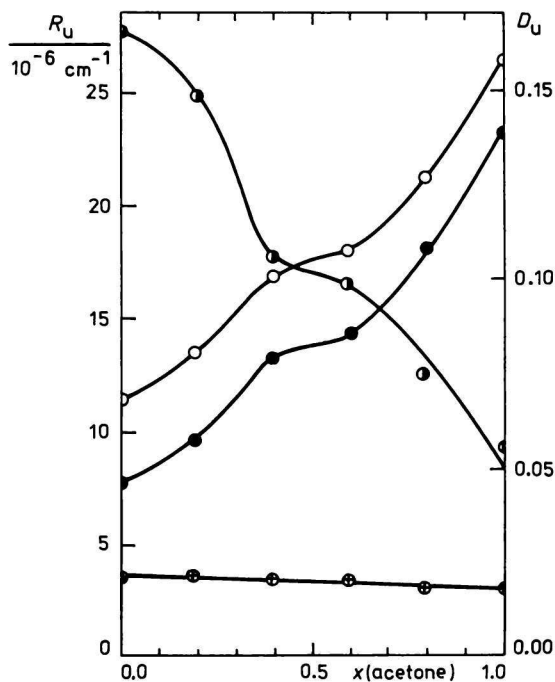


Fig. 2. Values of R_u^{ot} (\circ), R_u^{is} (\bullet), R_u^{anis} (\oplus) and D_u (\bullet) in the acetone—chloroform—PMMA mixture as a function of solvent composition at the constant concentration of PMMA (1.5 mg cm^{-3}).

course of other scattering characteristics is different. The curves exhibit discontinuities the analogues of which, from the viewpoint of localization, can be found in the paper published by *Dondos* [5] which deals with the viscosity of the acetone—chloroform—PMMA system or in paper [6] where *Fujishige* and *Elias* have presented their results obtained by investigating this system by the method of light scattering. The dependence of the limiting viscosity number of PMMA on composition of the binary solvent [5] is plotted in Fig. 3 while Fig. 4 represents the analogous dependence of the coefficient of preferential adsorption α , of the degree of expansion of polymer coil $\bar{s}_z/\bar{M}_w^{0.5}$, and of the secondary virial coefficient A_2 [6]. The last dependence does not exhibit any discontinuities, but the region of inflexion corresponds to the concentration interval where the mentioned discontinuities appear.

On the basis of these concords and interpretation of the information content of individual relationships we can state that not only the viscosimetric measurements but also the light scattering indicates the existence of conformational

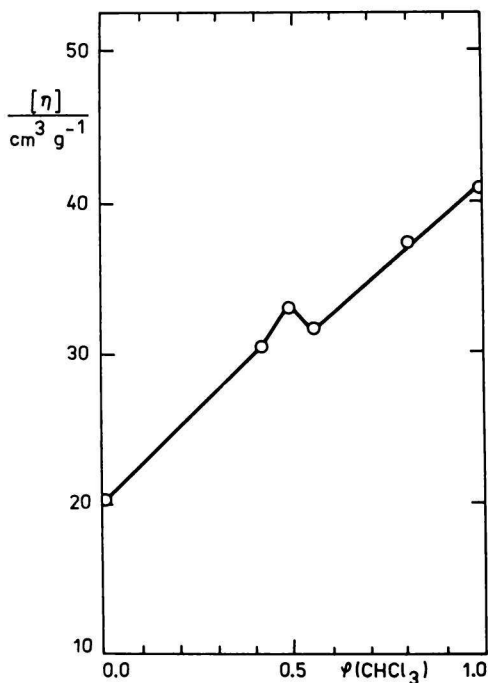


Fig. 3. Dependence of the limiting viscosity number $[\eta]$ of PMMA on composition of binary solvent in the PMMA—acetone—chloroform mixture [5].

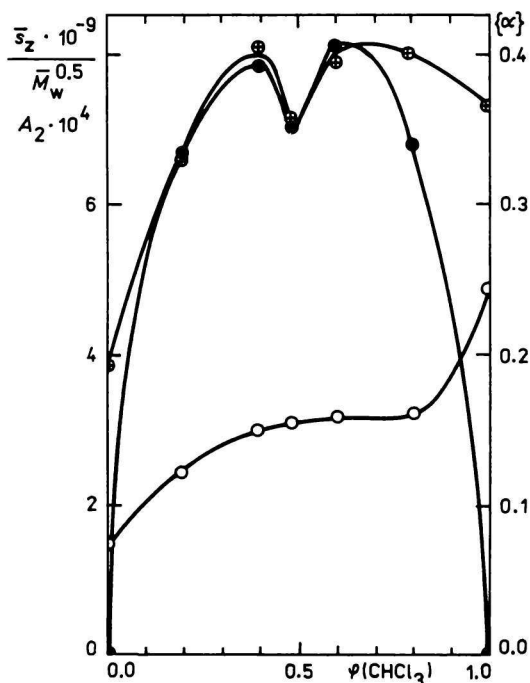


Fig. 4. Dependence of the values of A_2 (○), α (●), and $\bar{s}_z/\bar{M}_w^{0.5}$ (⊕) on composition of solvent in the PMMA—acetone—chloroform mixture [6].

transition in the investigated system. We may suppose that one ordered structure stable in one solvent passes into other organized structure stable in the second solvent. In the transition stage the polymer system exhibits disorder which is characterized by an increase in fluctuations of concentration and thus by an increase in the value of R_u^{ls} or R_u^{tot} .

Addendum: In paper [6] the mean values of molar mass \bar{M}_w /(g mol⁻¹), gyration radius \bar{s}_z^2 /cm², and secondary virial coefficient A_2 /(mol cm³ g⁻²) were determined by the Zimm method. In the case of mixed solvent we have to do with apparent values. The coefficient of preferential adsorption α is expressed by the equation $\alpha = n_1 V_1 / \bar{M}_w$ where n_1 and V_1 stand for number and partial molar volume of the solvent molecules preferentially adsorbed on polymer coil, respectively.

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