## Light scattering in the mixtures tetrahydrofuran— —dimethylformamide and tetrahydrofuran—dimethylformamide— —poly(vinyl chloride)

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The concentration dependence of the characteristics of light scattering was studied in the systems tetrahydrofuran—dimethylformamide and tetrahydrofuran—dimethylformamide—poly(vinyl chloride).

The character of the isotherm of the concentration light scattering in the tetrahydrofuran—dimethylformamide—poly(vinyl chloride) system has revealed the presence of specific interactions in the region of maximum solubility of poly(vinyl chloride) in the mixed solvent tetrahydrofuran—dimethylformamide. Simultaneously it has confirmed the assumption that the composition of the solvate sphere of macromolecules at their maximum solubility is identical with the composition of solvent among macromolecules.

Концентрационная зависимость основных характеристик рассеяния света была изучена в системах тетрагидрофуран—диметилформамид и тетрагидрофуран—диметилформамид—поливинилхлорид.

Ход изотермы концентрационного рассеяния света в системе тетрагидрофуран—диметилформамид—поливинилхлорид показал на присутствие специфических взаимодействий в области максимальной растворимости поливинилхлорида в смешанном растворителе тетрагидрофуран— —диметилформамид. Одновременно было подтверждено, что состав сольватной оболочки макромолекул при их максимальной растворимости соответствует составу растворителя в пространстве между макромолекулами.

Polymers in mixed solvents form different systems interesting from the theoretical as well as practical point of view. For instance, we may sometimes observe that the solvent mixture exhibits a greater thermodynamic affinity to macromolecules than its individual components alone. Since a useful information about the interactions in such systems may be also given by the method of light scattering

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[1-4], the topic of this study is the investigation of basic characteristics of light scattering in the mixtures THF--DMF and THF--DMF--PVC.

The estimation of the concentration dependence of individual scattering quantities has been based on the following relation [1]

$$\boldsymbol{R}_{u}^{\text{tot}} = \boldsymbol{R}_{u}^{\text{iso}} + \boldsymbol{R}_{u}^{\text{an}} \tag{1}$$

where  $R_u$  is the Rayleigh ratio for total, isotropic, and anisotropic light scattering and nonpolarized primary ray. While the isotropic contribution of the light scattered by liquid mixture may be regarded as a sum of fluctuations in density and concentration ( $R_u^{ino} = R_u^d + R_u^c$ ), the anisotropic scattering reflects the fluctuations in translation and orientation of anisotropically polarizable molecules.

## Experimental

The solvents were purified by twofold distillation in an efficient column. Tetrahydrofuran was subjected to action of KOH for several days and afterwards it was distilled with pure KOH and subsequently with metallic sodium. Commercial PVC Geon 121 ( $\overline{M_w} = 240\ 000$ ) was purified as described earlier [5]. Its solutions were prepared by weighing and dissolving PVC in mixed solvent. The purification of solvents and solutions was performed by means of pressure filtration through fritted glass filters G 5 (Schott, Jena) directly in measuring cells.

The light scattering was measured with a photogoniodiffusionmeter (Sofica) at the wavelength of 546 nm and  $25.0 \pm 0.2$  °C. Benzene was used as a standard for the calculation of individual scattering quantities ( $R_u^{\text{tot}} = 16.2 \times 10^{-6} \text{ cm}^{-1}$ ).

## **Results and discussion**

The scattering quantities of the investigated mixtures  $R_u^{iso}$  and  $R_u^{an}$  were calculated on the basis of experimental determination of total scattering  $R_u^{tot}$  and depolarization  $D_u = H_u/V_u$  by means of the following equations [1]

$$R_{u}^{iso} = R_{u}^{tot} \frac{(6-7D_{u})}{(6+6D_{u})}$$
(2)

$$R_{u}^{an} = R_{u}^{tot} \frac{13D_{u}}{(6+6D_{u})}$$
(3)

where  $H_u$ ,  $V_u$  are the Rayleigh ratios of the horizontally and vertically polarized components of scattered light. The values of these quantities obtained for different compositions of the DMF—THF mixture are given in Fig. 1.

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Fig. 1. Variation of the scattering quantities  $R_u^{uv}$ (O).  $R_u^{inv}$  ( $\Box$ ), and  $R_u^{un}$  ( $\nabla$ ) (10<sup>-6</sup> cm<sup>-1</sup>) with concentration in the THF—DMF mixture.  $x_1$  — mole fraction of tetrahydrofuran.

As known [1-4], the presence and type of molecular interactions may be ascertained from the character of the curve representing the concentration dependence of isotropic scattering. The mixtures with a positive or negative deviation from the Raoult law exhibit a maximum on the isotherms of isotropic scattering (the type of the deviation from ideality may be determined by comparing the concentration scattering with the so-called ideal scattering) while the presence of specific interactions (*e.g.* of the donor-acceptor type) manifests itself by a minimum on these curves [4, 6]. Provided the solutions are molecular mixtures (without associates and complexes), the isotherms of isotropic scattering have linear character. In this case, we are up against the systems containing components with similar molecular structure, *i.e.* comparable molecular dimensions or energies of interaction (hexane—pentane, hexane—octane, methanol—ethanol, *etc.*). As for the THF—DMF mixture, it is evidently a similar case if we judge the affinity of the components of mixture by the value of their solubility parameter  $\delta$  and hydrogen-bond index  $\Theta$  [7] which can have also a negative value

	$\delta (\rm J \ cm^{-3})^{1/2}$	$\boldsymbol{\varTheta}$
THF	41.4	12.0
DMF	50.6	18.9

Then the concentration dependences of  $R_u^{tot}$ ,  $R_u^{iso}$ , and  $R_u^{an}$  have monotonous, nearly linear course which points to the presence of weak interactions in this mixture. The results of infrared spectroscopy [8] are consistent with those facts because the absorption band of the carbonyl group of DMF in its 1% CCl<sub>4</sub> solution occurring at 5.925 µm shifts to 5.975 µm in CHCl<sub>3</sub> but only to 5.927 µm in the THF—DMF mixture.

Now let us observe the light scattering behaviour of the THF—DMF—PVC mixture (Fig. 2). As obvious, the  $R_{u}^{an}$  isotherm is practically identical with the



Fig. 2. Values of  $R_u^{\text{tot}}(\bigcirc)$ ,  $R_u^{\text{tot}}(\bigcirc)$ , and  $R_u^{\text{en}}(\nabla)$ (10<sup>-5</sup> cm<sup>-1</sup>) in the THF—DMF—PVC system as a function of composition of the THF—DMF solvent at a constant amount of PVC (1.5 mg cm<sup>-3</sup> of solvent).  $v_1$ —volume fraction of tetrahydrofuran.



Fig. 3. Values of  $R_u^{tet}(\bigcirc)$ ,  $R_u^{teo}(\square)$ , and  $R_u^{an}(\nabla)$ (10<sup>-5</sup> cm<sup>-1</sup>) in the THF—DMF—PVC system as a function of composition of the THF—DMF solvent at a constant amount of PVC (1.5 mg cm<sup>-3</sup> of solvent) after elimination of the solvent contribution.

 $v_1$  — volume fraction of tetrahydrofuran.

concentration dependence of  $R_{u}^{an}$  found for the THF-DMF binary mixture whereas the course of  $R_{\mu}^{tot}$  and  $R_{\mu}^{tot}$  is different from the course of analogous curves found for the binary mixture. The curve of  $R_{\mu}^{iso}$  passes through a minimum if the volume fraction of THF is equal to 0.35 while the value of  $D_{\mu}$  reaches a maximum in this region. The similarity between the  $R_{u}^{an}$  isotherms of both investigated mixtures is in harmony with observations that the anisotropic scattering due to the molecules of polymer is usually negligible. However, the presence of PVC macromolecules influenced the isotropic scattering and specific interactions polymer-mixed solvent appeared, which resulted in the formation of a minimum on the isotherm of isotropic scattering. Such a minimum was also observed with solutions of LiCl in alcohols and acetone [6] and in mixtures of pyridine with formic, acetic or propionic acid [4]. In both cited papers a formation of donor-acceptor bond owing to the dissociation of LiCl or carboxylic acids in particular solvents is assumed. The existence of this bond may be also supposed in the THF-DMF-PVC mixture because THF and DMF are solvents with a high electron-donor capacity. This statement is confirmed by the high solubility of PVC in the mixed solvent consisting of 35% THF and 65% DMF while only the mixture dimethylformamide—trimethylene oxide has similar dissolving ability [8].

According to Adelman and Klein [8], THF (in mixture with DMF) also contributes to the high solubility of PVC by the "voluminosity" of its molecule which is thus able to separate the polymer chains and reduce the forces inside them. From the optical point of view, we obtain a homogeneous system in which the fluctuations in concentration are minimum just in the region where the maximum solubility of PVC was found [8]. This fact is evident in Fig. 3 where the isotherms of "total", concentration, and anisotropic scattering of PVC (fluctuations in density have been eliminated by subtracting the flux of the light scattered by solvent) are represented. In addition to these observations, the method of light scattering has also confirmed the assumption that the composition of the solvate sphere of macromolecules in a system polymer—mixed solvent is identical with the composition of solvent in the space among macromolecules provided the maximum solubility of polymer has been reached.

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