SPECTROSCOPIC STUDY OF INTERMOLECULAR INTERACTIONS IN THE METHYL ACRYLATE — DIMETHYL SULFOXIDE SYSTEM

A. L. Bortnichuk, N. A. Bushuev, and N. N. Kornilova

The methyl acrylate — dimethyl sulfoxide system is a component part of many fiber-forming systems, particularly those used in the preparation of strengthened polyacrylonitrile fibers by the dimethyl sulfoxide method. Therefore, a study of the character of the intermolecular interactions in this system is important for the understanding of the processes which take place in the fiber-forming systems mentioned.

To obtain information about interaction of molecules in the methyl acrylate — dimethyl sulfoxide system we used the Raman light-scattering method. We used methyl acrylate (All-Union State Standard 15811-70) which had been purified by a threefold vacuum distillation ($n_2 1.3984$) and DMSO (of British manufacture) which had been purified by a double vacuum distillation ($n_2 1.4780$).

A study of the concentration dependence of the parameters of the Raman spectra (frequency, half-widths, and line intensities) of solutions of methyl acrylate in DMSO showed the following.

According to classical theory [1, 2] the Raman spectral linewidths should decrease with increase in solution viscosity. However, only the half-width of the 1735 cm$^{-1}$ line for the $q(C=O)$ stretching frequencies of methyl acrylate decreases with increase in DMSO concentration (increase in viscosity), while the 1293 and 1638 cm$^{-1}$ lines of methyl acrylate and the 1045 cm$^{-1}$ line of DMSO are broadened, the half-widths of the lines for the $q(S=O)$ stretching vibrations of DMSO (1045 cm$^{-1}$) and for the $r(HCC)$ deformation vibrations of methyl acrylate (1295 cm$^{-1}$) being changed more strongly.

The frequencies of most of the Raman lines of solutions of methyl acrylate in DMSO essentially are not changed with change in concentration of the solution, except for the frequency of the line for the $r(HCC)$ deformation vibrations of methyl acrylate, which decreases with increase in methyl acrylate concentration, and the frequency of the $q(S=O)$ stretching vibrations of DMSO, which increase with decrease in DMSO concentration (from 1045 cm$^{-1}$ in pure DMSO to 1070 cm$^{-1}$ at the maximum dilution of it with methyl acrylate). This type of frequency shift and change in contour of lines (half-widths) indicates the presence of direction intermolecular interactions in the methyl acrylate — dimethyl sulfoxide system and also indicates that the $q(S=O)$ vibrations of DMSO and the $r(HCC)$ vibrations of methyl acrylate experience a very large perturbation as a result of this interaction. Since the frequencies of the $q(S=O)$ vibrations increase with dilution, the intermolecular interactions involving $\pi$-electrons of this bond are greater in pure DMSO than in solutions of methyl acrylate. This conclusion is confirmed also by the behavior of the intensities of the main Raman lines of the solutions with change in concentration.

The dependence of Raman line intensities on change in methyl acrylate concentration in the solution does not obey the additivity law which ensures from the very nature of the phenomenon of Raman scattering [1, 3], but bears a nonlinear and complex character which is characteristic of solutions with a strong specific intermolecular interaction of the components [4-6]. The magnitude of the deviations of line intensities from additivity can readily be evaluated from the diagram of concentrations dependences of relative line intensities (Fig. 1), where the intensity of each line in the pure substance is taken as 100. The very magnitude of these deviations, in our opinion, can give information about the character of intermolecular interactions and, to a definite extent, about the structure of the complexes themselves.

Fig. 1. Concentration dependence of relative intensities of some lines in the Raman spectra of solutions of methyl acrylate in DMSO: Δν = 668 (1); 1045 (2); 698 (3); 344 (4); 858 (5); 1301 (6); 1734 (7); and 1642 cm⁻¹ (8).

Fig. 2. Most probable structure of methyl acrylate — dimethyl sulf oxide complex.

As a matter of fact, the intensities of Raman lines are determined by the polarizability (they are proportional to the square of the derivative of polarizability with respect to the normal coordinate) of a given molecule [3]. The polarizability of a molecule depends on the structure of its electron envelope and, consequently, on the distribution of electron density in its bonds. If there is a directed interaction of unlike molecules, then in the mutual overlap of the electron clouds of the interacting molecules it may turn out that the electron density in a given bond may be increased as compared with the pure substance, or it may be reduced, or it may remain approximately the same. This should lead to the situation that the intensity of a given line may prove correspondingly greater than in the pure substance (positive deviations from additivity), or less (negative deviations), or remain approximately the same (the additivity law is preserved — evidently characteristic only of mixtures of nonpolar molecules which are close in structure).

Then in a directed (specific) interaction a very large positive deviation from additivity (or a very small negative deviation) indicates a very large involvement of precisely this group of atoms in the molecule (their bonds and angles) in the interaction and can serve as a landmark to establish the structure of the complex.

Thus, negative deviations from additivity in the intensities of Raman lines of DMSO (Fig. 1) indicate that in pure DMSO there is a denser packing of the molecules (with a greater overlap of the electron clouds of neighboring molecules) than there is in a solution of methyl acrylate. Thereupon the form of association of the DMSO molecules varies with its dilution by methyl acrylate. Thus, at low methyl acrylate concentrations the q(S = O) bond, as well as the C — S = O internal angle, participates less in complex formation with methyl acrylate than the C — S bonds. At large dilutions, the extent of participation of the S = O bond in intermolecular interactions rises considerably, approaching that which is present in pure DMSO.

This is easy to understand by considering that in pure DMSO the dimeric associates [7] are united into grosser formations, interactions between whose fragments are weaker than those between two DMSO molecules in the dimers. Small additions of methyl acrylate break up these formations, but do not affect the dimers initially. Therefore, for a general negative deviation from additivity, the S = O bonds, being highly stressed in the dimers, participate weakly in interaction with methyl acrylate. At larger dilutions of the DMSO, even the dimers are broken up, and at this stage interaction with methyl acrylate molecules is accomplished with principal involvement of S = O bonds in mixed complexes. With small additions of methyl acrylate to DMSO, the deviations from additivity for the intensities of the Raman lines of methyl acrylate are small and positive, being approximately the same for all lines and being maximum at about 20% methyl acrylate. At this concentration there are four molecules of DMSO per molecule of methyl acrylate, which makes it possible to represent the complex easily either in the form of a tetrahedron inside of which there is a methyl acrylate molecule, with DMSO at the vertices, or as a laminar structure in which there is one molecule of methyl acrylate between two DMSO dimers. The latter structure seems preferable to use, since it does not require the dissociation of the two DMSO dimers.