

I. L. Fabelinskii, V. S. Starunov, A. K. Atakhodzhaev, T. M. Utarova, and G. I. Kolesnikov, *Narrowing of Optical Depolarization-Scattering Spectra Near the Critical Separation Point of Solutions*. Study of scattered-light spectra in the neighborhood of the critical point has yielded extensive information on the behavior of the correlation radius, compressibility, and thermal diffusivity of liquids, the mutual translational diffusion coefficients of solutions, the elastic constants of solids, and other properties of matter.

In our recent studies,<sup>[1-6]</sup> which the present paper describes, an attempt is made to study the temperature kinetics of the depolarized spectrum and thereby to establish the nature of the oriented motion of anisotropic molecules in the neighborhood of the critical separation point of solutions.

We studied the change in the width of the Rayleigh-line wing (RLW) due to anisotropy fluctuation and the change in the part of the depolarized Raman-scattering line (RSL) width that is due to oriented molecular motion and therefore of the same nature as the RLW.<sup>[7-9]</sup> Since the distribution of intensity in the RLW and RSL is of complex nature, study of the temperature kinetics of the depolarized spectrum requires an adequate method and careful reduction of the measurement results. In studying the RLW in solutions, we used six different Fabry-Perot standards with dispersion ranges from 62 to 1  $\text{cm}^{-1}$  to monitor the temperature kinetics on a certain segment (Lorentzian) of the RLW and thoroughgoing methods to reduce the measurement results.<sup>[1-6]</sup> In<sup>[5]</sup>,

we studied the possible misconceptions that can arise when an inadequate method of investigation is used. The intensity distributions in the RLW are described by two Lorentzians in pure liquids and by as many as three in solutions, not counting the remote part of the RLW, which is not described by a Lorentzian and was present in our experiments in the form of a continuous uniform background in the spectrum. The half-width  $\delta\omega$  of the corresponding Lorentzian is simply related to the anisotropy relaxation time:  $\tau = \delta\omega^{-1}$ . We studied the RLW in the following solutions: *n*-hexane-nitrobenzene,<sup>[1,2,5]</sup> *n*-dodecane- $\beta, \beta'$ -dichlorodiethyl ether,<sup>[2,5]</sup> *n*-hexadecane- $\beta, \beta'$ -dichlorodiethyl ether,<sup>[6]</sup> and carbon disulfide-ethyl alcohol.<sup>[3]</sup> In all of the cases studied, we observed a nonmonotonic narrowing of the RLW or an increase in the relaxation time  $\tau$  as the temperature approached the separation point. This narrowing of the RLW varies from one order of magnitude in the carbon disulfide-ethyl alcohol solution to several orders in the *n*-dodecane- $\beta, \beta'$ -dichlorodiethyl ether solution.

By way of example, Fig. 1 shows the temperature kinetics of  $\tau$  in an *n*-dodecane- $\beta, \beta'$ -dichlorodiethyl ether solution. The coordinates are  $\ln\tau$  and  $-\ln\varepsilon$ , where  $\varepsilon = (T - T_c)/T_c$ ;  $T_c$  is the critical temperature. In this example, we see three segments with rapid increase of  $\tau$ ; in other cases, there are two of them, and there is only such segment in the case of the carbon disulfide-ethyl alcohol solution.

We studied the temperature kinetics of the depolarized 656  $\text{cm}^{-1}$  line of carbon disulfide in the carbon di-

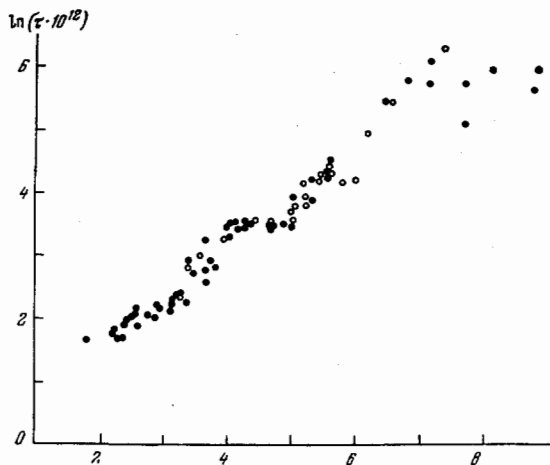


FIG. 1. Plot in  $\ln\tau$  against  $-\ln\epsilon$  in mixture of *n*-dodecane and  $\beta, \beta'$ -dichlorodiethyl ether.

sulfide-ethyl alcohol solution and of the 610, 1345, and 1586  $\text{cm}^{-1}$  lines of nitrobenzene in the nitrobenzene-*n*-hexane solution. The results of these studies appear in Fig. 2. Here the half-widths  $\delta\nu$  of the RSL are plotted against  $T/\eta$  ( $\eta$  is the shear viscosity) and  $T - T_c$ . Figure 2 shows an anomalous narrowing of the RSL or an increase of  $\tau$  with the approach to the critical temperature in both solutions and for all of the depolarized lines studied. The narrowing of the 656  $\text{cm}^{-1}$  line keeps pace with the narrowing of the RLW in this solution, and their temperature dependences agree. The 1345 and 1586  $\text{cm}^{-1}$  lines are also narrowed by practically the same factor as the RLW in this solution; it is possible that the anomalous narrowings of these lines in various temperature ranges are related to the various segments on which the RLW show nonmonotonic narrowing. It was verified experimentally that none of the RSL studied has singularities in noncritical solutions.

If the ranges of rapidly increasing  $\tau$  or narrowing of  $\delta\omega$  and  $\delta\nu$  are described by the formula  $\tau = (A + B\epsilon^\sigma)^{-1}$ , it is easily found, e. g., for the carbon disulfide-ethyl alcohol solution, that the critical exponent  $\sigma = 2$  for the RSL and RLW. The same critical-exponent value is obtained for both segments of rapidly increasing  $\tau$  for the RLW of the *n*-hexane-decane and *n*-dodecane solutions in  $\beta, \beta'$ -dichlorodiethyl ether.

The report discusses the experimental results from

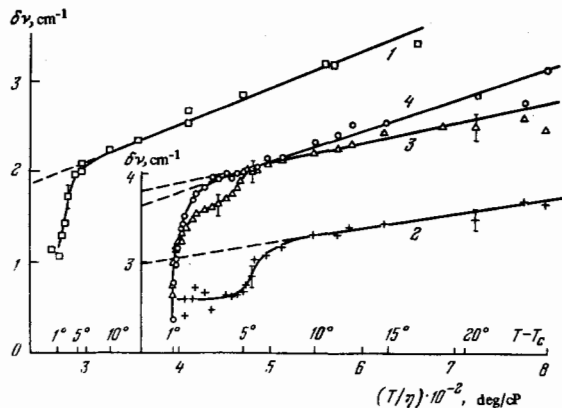


FIG. 2. Half-width of 656  $\text{cm}^{-1}$  Raman scattering line of carbon disulfide in carbon disulfide-ethyl alcohol mixture (1) and 610  $\text{cm}^{-1}$  (2), 1345  $\text{cm}^{-1}$  (3), and 1586  $\text{cm}^{-1}$  (4) lines of nitrobenzene in nitrobenzene-*n*-hexane mixture vs  $T - T_c$  and  $T/\eta$ .

the standpoint of theories that predict narrowing of the depolarized scattered light spectrum.

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