DISTRIBUTION OF IMPURITY MOLECULES IN POLYCRYSTALLINE n-PARAFFIN SOLVENT IN THE CASE OF QUASILINE SPECTRA

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One of the most important questions arising in any discussion of the nature of the Shpol'skii effect [1] is the distribution pattern of impurity molecules in the polycrystalline matrix formed when the investigated solution freezes.

That topic has been investigated earlier by several authors [2-9]. Several assumptions as to the nature of the impurity centers responsible for the quasiline spectra were put forth. For example, some of the authors [2-5] concluded, on the basis of investigations of concentration dependences of the spectra and the sensitized fluorescence, that individual impurity molecules present in the crystalline matrix of the solvent are responsible for the quasiline spectra. It is suggested [6] that the quasiline spectra can be produced by impurity molecules adsorbed on the surfaces of microcrystals in the polycrystalline n-paraffin matrix. It has also been suggested [7, 8] that the quasiline spectra are yielded by aggregates of impurity molecules. Another inference [9] is that the impurity centers located within the microcrystals of the polycrystalline matrix yield the quasiline spectra; here the inference is based on investigations of temperature quenching of fluorescence.

We made a study of the distribution pattern of 3, 4-benzopyrene and dibenzoperopyrene impurity molecules [10] in polycrystalline n-octane matrix.

When the solution crystallizes, impurity molecules can either enter the crystal lattice of the n-paraffin, or can be forced out of the polycrystals of the polycrystalline matrix, into the space between crystallites or into various microcracks. If the impurity molecule enters the crystal lattice, then, first, it can lodge at a lattice point, forcing out one molecule of the host matrix in the process, or, second, it can end up between lattice points, or, third, when the dimensions of the molecule are much larger than the dimensions of the host matrix molecule, it can occupy several lattice sites, forcing out the corresponding number of host lattice molecules as it does so. And finally, as pointed out by Shpol'skii [1], an inclusion compound [11] could form. Inclusion compounds comprise a two-component system in which molecules of one species are found in cavities formed by the molecules of the other species. The dimensions of the hole or cavity are close to the dimensions of the accommodated molecule, so that the latter is held more or less rigidly in place. It is also significant here that the cavities are capable of forming when the system components crystallize jointly, since they cannot exist in a single-component crystal lattice.

It can be assumed that (as is the case in some inclusion compounds that have been studied) cavities with dimensions close to the dimensions of the impurity molecule, and in which the impurity molecules are oriented in a specific way, form in the n-paraffin lattice when a solution of an organic molecule in n-paraffin crystallizes.

Accordingly, we must first solve the problem of whether the impurity molecules yielding the quasiline spectrum are located within microcrystals of the polycrystalline n-paraffin matrix or whether they are forced out into the intercrystallite space on the surface of such microcrystals. We therefore conducted the following experiments (the experimental procedure followed is similar to one described by Butlar [6]). n-Octane was precipitated onto a pin cooled by liquid nitrogen and placed within an evacuated volume (p = 10^-5 mm Hg). The impurity to be investigated was then sputtered onto the resulting crystalline n-paraffin surface. The octane was admitted to the evacuated volume via a capillary tube, and the rate of precipitation...
of the n-octane could be varied by varying the diameter of the capillary. The impurity was sputtered into place with the aid of a special heater and the sputtering rate was determined by the heating temperature. The impurity and the n-octane were taken in amounts corresponding to $10^{-5}$ impurity concentration in the n-octane.

The sputtering was achieved in several different ways. In the first series of experiments, the n-octane was deposited first, and the impurity was then sputtered over the surface of the n-octane substrate. In that experiment, and in all subsequent experiments, the sputtering of the material was terminated immediately after emission was observed (the surface of n-octane was illuminated during the sputtering process by a PRK-4 mercury lamp through a UFS-4 filter). Simultaneous deposition of n-octane and sputtering of the test material was carried out in a second series of experiments. In a third series of experiments, a thin layer of n-octane was deposited, after which the impurity was sputtered on, then more n-octane was deposited, and then again impurity was sputtered onto the surface of that n-octane, and so on until luminescence appeared.

The point of the second and third series of experiments was as follows. It is possible that the luminescence recorded in the first series of experiments was due to emission not from a monolayer of impurity molecules, but from a thicker coating (luminescence of a monolayer can be very weak, so that its detection can present difficulties). At the same time, it may be assumed that the quasiline spectra derive from molecules forced out in the usual method of freezing of the solution into the intercrystallite space, and ending up on the surfaces of the microcrystals in the form of a monolayer (in this case the luminescent emission is intense, since it is observed from the entire volume of a polycrystal with a highly developed surface). This uncertainty is evidently eliminated in the second and third series of experiments. In those experiments the rates of deposition of a n-octane and of sputtering of impurity were varied over wide ranges. In particular, the impurity was sputtered in one of those experiments for a full hour prior to the appearance of luminescence. The same results were obtained in all three series of experiments.

Photoelectric traces of the luminescent emission spectrum of 3, 4-benzopyrene at $T = 77^\circ$K, as sputtered by the three contrasting methods onto the surface of n-octane, are shown in Fig. 1. For comparison, quasiline spectrum of the luminescence of 3, 4-benzopyrene in n-octane obtained when the solution froze quickly, and a spectrum of 3, 4-benzopyrene in ethyl alcohol vitrifying upon freezing, are shown also in Fig. 1. (The spectra were recorded with a DFS-12 spectrometer, and the luminescence was excited by a DRSh-250 mercury lamp through an UFS-4 filter.) Clearly, the luminescence spectrum of 3, 4-benzopyrene sputtered onto the surface of n-octane is not a quasiline spectrum. That is evidence that the impurity molecules responsible for the quasiline spectrum are found not on the surfaces of microcrystals of the n-paraffin matrix, but within those microcrystals. Since the dimensions of the 3, 4-benzopyrene molecule are far greater than the dimensions of the n-octane molecule, it is evident that the 3, 4-benzopyrene molecule cannot fit into the n-octane crystal lattice site. What is most likely is that the impurity molecule becomes accommodated within the cavity formed in the n-octane crystal lattice when the n-octane and the impurity crystallize jointly.

For further elucidation of the distribution pattern of the impurity molecules in the polycrystalline n-paraffin matrix, experiments were conducted to determine the effect of the rate of crystallization of the solution on the form of the quasiline spectrum. A long thin-walled capillary cell containing a solution of