characteristics of the change in the concentration factor established by the calculations are also qualitatively manifested in  $C_e^e$ . Thus the measurements imply that for LSC of the same size (62 mm) the most efficient ones are quartz glass LSC activated with Sm<sup>2+</sup>, for which  $C_e^e$  is one and a half times higher than for polymer samples with R6G. With their use the power of the electric current generated by a 24 × 2 mm PVC increases by a factor of 3.5.

The very strong effect of the immersion liquid between the end face of the LSC and PVC on the value of  $C_e$  should also be noted. Table 2 shows that  $C_e^e$  is 2.5 times lower in the absence of the immersion liquid.

The agreement between the computed and experimental values of  $C_e$  indicates that the computational scheme used and the assumptions adopted are adequately justified and such calculations can be employed for selecting optimal LSC. For example, the calculations imply that lowering the losses in glasses with  $Sm^{2+}$  to a level characteristic for polymer samples would permit increasing for the same dimensions of the LSC the concentration factor  $C_e$  from 3.5 to 5.3.

The authors are grateful to M. V. Braslavskaya for assistance in some of the experiments.

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PMR-, IR-, AND UV-SPECTROSCOPIC STUDIES OF PRODUCTS OF REACTION OF DICYANDIAMIDE WITH FORMALDEHYDE. METHYLOL AND METHYLENE ETHER DERIVATIVES

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UDC 543.422:547.288

Amido- and amino-formaldehyde resins comprise an important class of polymers. These products, which are based on carbamide, aniline, and melamine, have long been used on an industrial scale [1]. However, only in the last 10-15 years, because of the wide application of spectral and chromatographic methods of research, has considerable progress been achieved in the clarification of their molecular composition and of the structure of individual components, and in the understanding of processes on which their preparation and curing is based. The least investigated are the dicyandiamide-formaldehyde resins (DFR), whose use is promising for the preparation of hydrophobic, fireproof and other polymers. There is practically no information in the literature on the spectral characteristics of DFR.

The primary products in the reaction of dicyandiamide (I) with formaldehyde in a neutral or a weakly alkaline medium are methylol derivatives, of which monomethylol (II) and dimethyloldicyanamide (III) were isolated in a pure state [2]:

Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 46, No. 3, pp. 437-441, March, 1987. Original article submitted November 6, 1985.



Fig. 1. PMR spectrum in DMSO-d<sub>6</sub> of: dicyandiamide (1); monomethyloldicyanamide (2); dimethyloldicyandiamide (3) monomethoxymethyldicyanamide (4) and dimethoxymethyldicyandiamide (5). The signals with  $\delta =$ 2.50 and 3.47 ppm belong to the residual proton of the solvent and water, respectively.

Fig. 2. Ultraviolet spectra of monomethyloldicyandiamide (1), dimethyloldicyandiamide (2), monomethoxymethyldicyandiamide (3) and dimethoxymethyldicyandiamide (4) in water.

$$N \equiv C - N = C < NH_{2} + CH_{2}O \rightarrow N \equiv C - N = C < NHCH_{2}OH I II N \equiv C - N = C < NHCH_{2}OH NHCH_{2}OH + CH_{2}O \rightarrow N \equiv C - N = C < NHCH_{2}OH NHCH_{2}OH NHCH_{2}OH . (2) III$$

The methylol groups react with methanol in an acid medium, forming mono- (IV) and dimethoxymethylenedicyanamide (V) [3]:

 $N \equiv C - N = C < NHCH_2OCH_3 \\ N \equiv C - N = C < NH_2CH_2OCH_3 \\ NHCH_2OCH_3 \\ V$ 

To identify the main structural groupings, we studied in the present work the PMR, IR, and UV spectra of compounds II-V, synthesized by known methods [2-4].

The PMR spectra of 10-15% solutions of samples in dimethyl sulfoxide-d<sub>6</sub> (DMSO-d<sub>6</sub>) were recorded on a BS-487 C "Tesla" spectrometer (working frequency 80 MHz), using tetramethylsilane as internal standard. The chemical shifts are given on  $\delta$ -scale with an accuracy within  $\pm 0.01$  ppm. The IR spectra of the solid samples, pressed with KBr, and of the resinlike products in the form of a film between Ge glasses were recorded on a UR-20 spectrophotometer.

The UV spectra of the aqueous solutions of the compounds studied were measured on a SF-16 spectrophotometer.

The composition of compounds II-V was confirmed by elemental analysis carried out an a CHN-3 analyzer. For II  $C_{3}H_{6}ON_{4}$  (114), calculated (%) C 31.58, H 5.26, N 49.12; found (%) C 31.6, H 5.3, N 48.9; for III  $C_{4}H_{8}O_{2}N_{4}$  (144), calculated C 33.33, H 5.59, N 38.87, found C 32.7, H 5.8, N 38.0; for IV  $C_{4}H_{8}ON$  (128), calculated C 37.49, H 6.29, N 43.72, calculated C 37.0, H 6.3, N 42.9; for V  $C_{6}H_{12}O_{2}N_{4}$  (172) calculated C 41.85, H 7.03, N 32.54, found C 41.1, H 6.9, N 32.5.



Fig. 3. IR spectra of monomethyloldicyandiamide (1), dimethyloldicyanamide (2), monomethoxymethyldicyandiamide (3), and dimethoxymethyldicyandiamide (4).

TABLE 1. Chemical Shifts ( $\delta$ , ppm) and Spin-Spin Coupling Constants (J, Hz) in PMR Spectra of Dicyandiamide and Formaldehyde Derivatives

Compound	ô <sub>NH₂</sub>	δ <sub>NH</sub>	<sup>8</sup> он	δ <sub>CH2</sub>	<sup>8</sup> CH₃	<sup>Ј</sup> сн <sub>2</sub> —он	J <sub>CH3</sub> —NH
I III III IV V	6,57 6,83 6,97	7,33 7,63 7,64 8,02	5,64 5,73	4,504,564,474,53	 3,18 3,20	6.5 	6,5 6.7 6,45

In the PMR spectra of the compounds studied (Fig. 1), bands are observed, belonging to the main proton-containing structural groupings in the regions: 6.5-7.0 ppm (-NH<sub>2</sub>), 7.3 ppm ( $\rightarrow$ NH), 5.6-5.8 ppm ( $\rightarrow$ OH), 4.5-4.6 ppm ( $\rightarrow$ CH<sub>2</sub> $\rightarrow$ ) and 3.1-3.2 ppm ( $\rightarrow$ CH<sub>3</sub>) (Table 1). The signals of the  $\rightarrow$ NH-,  $\rightarrow$ OH- and CH<sub>2</sub>-groups are split into a triplet because of a spin-spin interaction whose constants are given in Table 1.

For dimethyloldicyandiamide (III), the form of the spectrum does not change in the course of time. There is a certain broadening and decrease in intensity of the bands, and an absorption band of the  $NH_2$ -group appears. These changes are due to the dissociation of III to II and formaldehyde [3] and indicate that in the solvent, the equilibrium of reaction (2) is shifted to the left.

The readily occurring reversible dissociation of the dimethylol derivative in water, compared with the urea and melamine analogs, makes it impossible to measure PMR spectra in  $D_2O$  [5]. To avoid superposition of signals of the  $CH_2$ -protons and the averaged signal of the HDO-,  $NH_2$ -,  $NH_-$  and OH protons, we must measure the spectrum at 80-90°C. In this case the spectrum characterizes the composition of the equilibrium reaction mixture and not of the starting compounds.

Substitution of hydrogen in the amino group by the methylol group -CH<sub>2</sub>OH- or the methyleneether group -CH<sub>2</sub>-O-CH<sub>3</sub> group leads to a shift of all the bands into a weak field, whereby the signal of the NH-proton in the group being substituted undergoes the greatest shift. Because of the great distance of the amino groups from one another, the influence of substituting groups on the chemical shift of the NH-proton accumulates additively. In fact, the contributions of the metholol group to the chemical shift of the amino group proton relative to dicyandiamide, calculated from the spectra of compounds II and I, are  $a_{\rm m}^{(1)} = 0.76$  ppm and  $a_{\rm m}^{(2)} = 0.26$  ppm for the first and the second amino groups, respectively, and gives the calculated value  $\delta_{\rm NH}$  for III equal to 7.59 ppm, which coincides, within the experimental error, with the observed value (Table 1). Similar contributions of the methylene-ether group are:  $a_{\rm me}^{(1)} = 1.07$  ppm and  $a_{\rm me}^{(2)} = 0.40$  ppm.



Fig. 4. PMR spectrum in DMSO-d<sub>6</sub> of a dry dicyandiamideformaldehyde resin.

Similarly, in the UV spectra of compounds II-V (Fig. 2), compared with I for the long-wave absorption band ( $\lambda_{max} = 215$  nm,  $\varepsilon = 13,600$  [6]), belonging to a singlet transition of the <sup>1</sup>A symmetry [7], the bathochromic shift increases additively. The additive shifts relative to I for the methylol and methylene-ether groups are equal to 3 and 4 nm, respectively. In contrast, the influence of these substituting groups on the extinction coefficient is opposite, and namely, for the methylol derivatives II and III a hyperchromic, and for the methylene-ether derivatives IV and V a hypochromic effect is observed.

The most characteristic absorption band in the IR spectra of dicyandiamide derivatives II-V (Fig. 3) is the intense band at 2180 cm<sup>-1</sup>, belonging to the stretching vibration of the nitrile group ( $v_{C \equiv N}$ ) group. In (1), this band is split into two components as the result of Fermi resonance with extraplanar vibration  $\gamma_{NH_2}$  [7]. In the spectra of the compounds II-IV studied, this band is split because of disturbances in the resonance conditions. In the stretching vibrations region of the NH- and OH groups of compounds II-V, several bands are observed, in the assignment of which serious difficulties are encountered, except for the ether derivative V, in which the affiliation of the only observed band in this region at 3300 cm<sup>-1</sup> to the stretching vibration of the NH group does not cause any doubts.

In the spectra of compounds II-V, in the  $1500-1700-cm^{-1}$  region, depending on the presence of NH<sub>2</sub> groups in them, three bands (1645, 1600, and 1580 cm<sup>-1</sup> for II and 1683, 1632, and 1555 cm<sup>-1</sup> for IV) or two bands (1625 and 1590 cm<sup>-1</sup> for III and 1605 and 1572 cm<sup>-1</sup> for V) are observed. This gives reason, in the group frequencies approximation, to assign these bands to deformational vibrations of the NH<sub>2</sub> and NH groups and to stretching vibrations of the C=N group in the first case, and to the NH and the C=N group vibrations, respectively, in the second case.

It is known that the deformational vibrations of the OH group are not very characteristic because of a strong bond with stretching vibrations of the C-O grouping [8]. However, in alcohols, there is a band in the  $1300-cm^{-1}$  region, which in several cases is related to the vibration of the hydroxyl group [9]. In methylol derivatives II and III there are bands at 1283 and 1275 cm<sup>-1</sup>, respectively, which can be related to the deformational vibrations of the OH group, since this band is absent in the corresponding ethers IV and V. Moreover, during the deuteration of II, the 1283-cm<sup>-1</sup> band disappears, and a new band at 920 cm<sup>-1</sup> appears.

From the study of the spectra of DFR, certain conclusions can be made on their composition. The DFR obtained by the reaction of the dimethylol derivative III with formalin at 60-70°C, followed by vacuum distillation of excess water, contained 40% of I, 48% of CH<sub>2</sub>O and 12% of H<sub>2</sub>O, based on the starting materials (determined from the integral intensities in the PMR spectrum), and consisted of a viscous colorless liquid, from which on drying in air a vitreous polymer was obtained. In the PMR spectrum of the polymer (Fig. 4), the most intense band was that of the CH<sub>2</sub>-protons, lying in the 4.6-5.6-ppm region. Proton signals of water are observed (3.47 ppm) and of the methyl group of the products of the reaction of the methylol derivatives and formalin with methanol (3.20-3.25 ppm). In the resonance region of the "mobile" protons, the most intense was the band of the NH-protons, while the NH<sub>2</sub> group signals are almost absent, and the OH groups give a weak absorption at 5.2-5.9 ppm. In the IR spectrum of the polymer, the NH<sub>2</sub> deformational vibrations band is absent in the 1600-1700-cm<sup>-1</sup> region, and the weak absorption in the 1200-1300-cm<sup>-1</sup> region indicates that the content of the hydroxyl groups in this region is insignificant. The above facts show that the polymerization of DFR proceeds mainly with the formation of methylene-ether bridges, and the methyl groups remain as the terminal groups. This is indicated by the high content of oxygen in the polymer - 26.6% (determined in a CHN-3 analyzer). It should be noted that in [10] the 830 cm<sup>-1</sup> band is indicated, together with the 2810 cm<sup>-1</sup> band, as the most characteristic for DFR. We did not observe this band in the IR spectra of neither the aqueous or anhydrous DFR.

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## CALCULATION OF FREQUENCIES AND INTENSITIES IN THE IR ABSORPTION SPECTRUM OF POLY(TETRAFLUOROETHYLENE)

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UDC 535.34

Among the vibrational spectra of polymers, the spectrum of poly(tetrafluoroethylene) (PTFE) is of special interest for theoretical analysis. Kinematically the molecule of this polymer,  $-(CF_2-CF_2)n-$ , differs significantly from the most spectrally studied and structurally analogous polyethylene molecule because the substituents which are at the "periphery," fluorine atoms, have a higher mass than the carbon atoms comprising the backbone. As a result of this, to a significant degree the molecule vibrates because of displacement of carbon atoms.

The spectra of PTFE were considered in [1-6], and their vibrations were assigned. However, in these papers there is not calculation of the intensities of the spectral bands, and the vibrations of rotational isomers are not analyzed. The interpretation of the spectra of PTFE was based on the assumption of a weak effect of intermolecular interactions on these spectra [4, 6]. At the same time, the observed vibrational spectra of PTFE have a number of characteristics not yet satisfactorily explained. Together with the doubling of the IR bands at 640-625  $cm^{-1}$  and the Raman lines at 595-575  $cm^{-1}$  repeatedly discussed in the literature [3-5], we note the large half-width and complex shape of the absorption bands near 1210 (halfwidth of about 52 cm<sup>-1</sup>) and 520 cm<sup>-1</sup> (half-width of 25-35 cm<sup>-1</sup>) and also the relation of the shape of these bands to the method of sample preparation. It is possible to enumerate a series of possible reasons for the appearance of wide bands in the polymer spectrum: intensity distribution with respect to the frequency branch of the polymer vibrations, superposition of bands assigned to different vibrations, superposition of absorption bands of different conformers, and intermolecular interactions. For quantitative evaluation of the effect of the enumerated factors on the polymer spectrum, it is necessary to calculate the frequencies and intensities in the vibrational spectra of the PTFE models.

The results of theoretical analysis of the vibrational spectra of molecules appearing in the homologous series of n-perfluoroparaffins served as the basis for such calculation. As a result of combined solution of the spectral problems for the molecules  $C_2F_6$ ,  $C_3F_6$ ,  $n-C_4F_{10}$ , and  $n-C_6F_{14}$  we chose the values of the force and electrooptical parameters for the CF<sub>3</sub> and

Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 46, No. 3, pp. 442-446, March, 1987. Original article submitted October 17, 1985.