NMR study of the phenol—formaldehyde—water—methanol system

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A quantitative evaluation of the system phenol—formaldehyde—water—
—methanol was carried out by the method of ^{1}H-n.m.r. spectroscopy. The
interested region of the molar ratios phenol—formaldehyde—methanol varied
within the range $1:29:9.6$—$1:0.2:0.07$ and the spectra obtained were com-
pared with the spectrum of water—methanol solution of formaldehyde. The
system showed two groups of lines. Four simple singlets of linear polymers of
the type $C_6H_5O(CH_2O)_nH$ appeared in the region 5.20—$5.35\ \delta$ whereas in the
region 4.7—$5.4\ \delta$ as many as eleven signals of the polymers $HO(CH_2O)_nH$ and
$CH_3O(CH_2O)_nH$ could be detected. Another three signals of polymers of the
type $C_6H_5O(CH_2O)_nCH_3$ appeared in the region 4.8—$5.0\ \delta$ from the molar
ratio phenol—formaldehyde $1:2.2$.

При помощи спектроскопии ЯМР была количественно рассмотрена
система фенол—формальдегид—вода—метанол. Молярные отношения
фенол—формальдегид—метанол менялись в пределах от $1:29:9,6$ до
$1:0,2:0,07$ и полученные спектры ЯМР были сравнены со спектром
водно-метанольного раствора формальдегида. В системе наблюдались две
группы линий. В области $5,20$—$5,35\ \delta$ обнаружены четыре простых
синглета линейных полимеров типа $C_6H_5O(CH_2O)_nH$ и в области
$4,7$—$5,4\ \delta$ до 11 сигналов полимеров $HO(CH_2O)_nH$ и $CH_3O(CH_2O)_nH$.
Начиная с молярного отношения фенол—формальдегид $1:2,2$ в области
$4,8$—$5,0\ \delta$ появляются дальнейшие три сигнала полимеров типа
$C_6H_5O(CH_2O)_nCH_3$.

Phenol-formaldehyde resins do not frequently reach required properties and the
production has to solve different problems involving the influence of methanol in
an aqueous solution of formaldehyde on the course of synthesis and properties of
the product. The stabilizing effect of methanol on aqueous solution of formal-
dehyde from the view-point of ensuring a low molecular weight of the hydrated
form of polymeric formaldehyde has been described [1, 2]. Its presence in an
aqueous solution of formaldehyde is also necessary for the transport of this raw
material. However, it is also known that it has unfavourable influence on the

properties of the product and the prolongation of curing time of the moulding powders prepared from these resins [3].

The ^{1}H-n.m.r. spectra of the system phenol—formaldehyde—water—methanol obtained with molar ratios of phenol to formaldehyde $1:29$—$1:0.2$ are more complicated when compared with the spectra of a system without methanol. This system exhibits only signals of the protons of the methylene groups of the polymers $HO(CH_2O)_n H$ and $C_6H_5O(CH_2O)_n H$ in the region 4.7—5.4 δ [4]. In the system containing methanol another group of lines appears in this region corresponding to the polymers $CH_3O(CH_2O)_n H$.

A different shift of signals of the methylene groups of the polymers $HO(CH_2O)_n H$ and $CH_3O(CH_2O)_n H$ and their distribution in two groups of spectral lines are due to different shielding of these protons by vicinal functional groups. As the influence of substituents is additive, the position of signals of differently shielded protons of the methylene groups may be predicted with sufficient accuracy by means of the Shoolery effective constants of shielding corresponding to the given substituent [5]. At the same time the influence of different magnetic susceptibility of the system measured by means of external standard must be taken into consideration.

The aim of this study is to make a basis for the investigation of the initial degree of condensation of phenol with water—methanol solution of formaldehyde under different conditions especially if different types of catalyst and different molar ratios of the starting components are used.

The evaluation of spectra has been performed on the basis of papers [4, 6, 7] by combining integral records and planimetric procedure.

Experimental

The spectra of the system phenol—formaldehyde—water—methanol were run on a Tesla 487 A (80 MHz) instrument. The measurement temperature was 80°C and hexamethyl disiloxane in a sealed capillary was used as an external standard. The samples were prepared from water—methanol solution of formaldehyde containing 36.9 weight % of formaldehyde and 12.27 weight % of methanol.

The cumene phenol used was purified by fractional distillation. The purity of the water—methanol solution of formaldehyde was checked by determining the content of formic acid which was lower than 0.01% by weight.

Results and discussion

The fundamental ^{1}H-n.m.r. spectrum of water—methanol solution of formalde-hyde has been described [6]. Provided a high resolution is secured, another four signals appear together with the original seven lines (Fig. 1). The assignment of
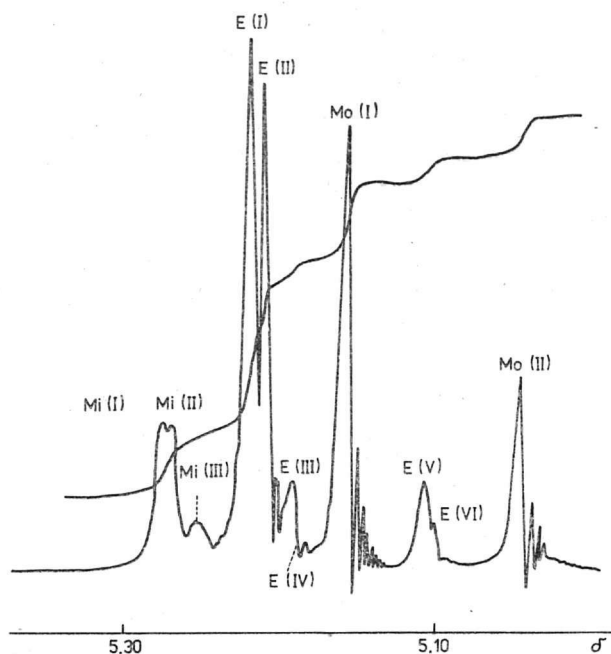
Fig. 1. ^{1}H-n.m.r. spectrum of water—methanol solution of formaldehyde.

individual lines of this spectrum to the protons of the methylene groups of linear polymers of the general formulae $HO(CH_2O)_n H$ (*I*) and $CH_3O(CH_2O)_n H$ (*II*) will be given later. If phenol is present in the system, the chemical shift of the signals of the methylene protons of individual structures changes. A spectrum for the molar ratio phenol : formaldehyde : methanol $1 : 29.18 : 9.63$ is presented in Fig. 2 (signal E(IV) is overlapped by signal Mo(I)). The assignment of the protons of the methylene groups to polymer *I* and *II* in the sense of increasing magnetic field is as follows

δ_1 —Mi(I)   middle groups of polymer *I* —O—CH_2—O— for $n = 3$
δ_2 —Mi(II)   middle groups of polymer *I* —O—CH_2—O— for $n \geqq 4$
δ_3 —Mi(III) middle groups of polymer *II* —O—CH_2—O—
δ_4 —E(I)   end groups of polymer *I* HO—CH_2—O— for $n = 2$
δ_5 —E(II)   end groups of polymer *I* HO—CH_2—O— for $n \geqq 3$
δ_6 —E(III)   end groups of polymer *II* HO—CH_2—O— for $n = 2$
δ_7 —E(IV)   end groups of polymer *II* HO—CH_2—O— for $n \geqq 3$
δ_8 —Mo(I)   hydroxymethanol HO—CH_2—OH
δ_9 —E(V)   end groups of polymer *II* CH_3O—CH_2—O— for $n = 2$
δ_{10}—E(VI)   end groups of polymer *II* CH_3O—CH_2—O— for $n \geqq 3$
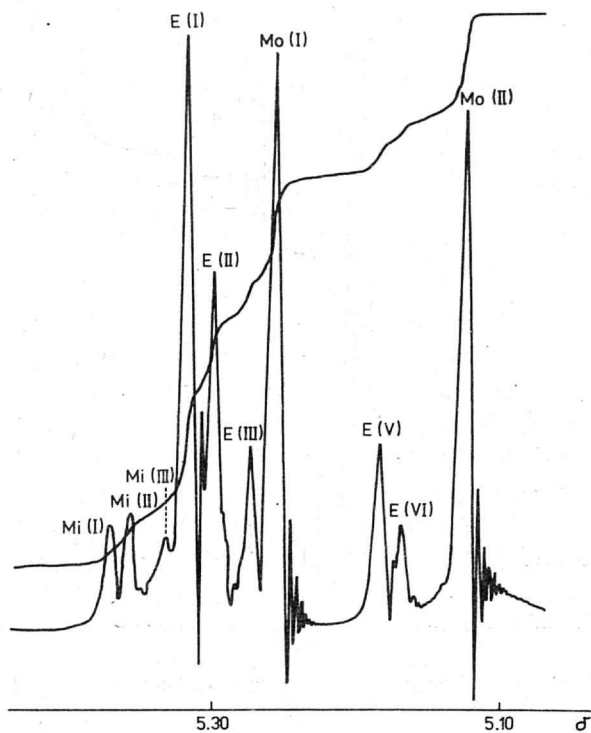δ_{11}—Mo(II) methoxymethanol CH_3O—CH_2—OH

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Fig. 2. ¹H-n.m.r. spectrum of water—methanol solution of formaldehyde with phenol.
The number of moles of formaldehyde and methanol per 1 mole of phenol is 29.18 and 9.63, respectively.

An increase in the content of phenol of the water—methanol solution of formaldehyde up to the molar ratio phenol : formaldehyde 1 : 2.2 does not change the multiplicity of spectrum but the width of spectrum, position, and order of signals change. At the above molar ratio of phenol to formaldehyde a group of four lines of the methylene protons of linear polymers $C_6H_5O(CH_2O)_nH$ (*III*) starts to appear in lower magnetic field (5.20—5.35 δ). The intensity of the right couple of signals of this multiplet is, however, very small in comparison with other lines of spectrum and therefore in quantitative analysis its value may be considered equal to zero. In contrast to the spectra of the solutions containing phenol, formaldehyde, and water it does not show any increase if the content of phenol in the system rises (Fig. 3). The assignment of these four signals to the protons of the methylene groups is as follows
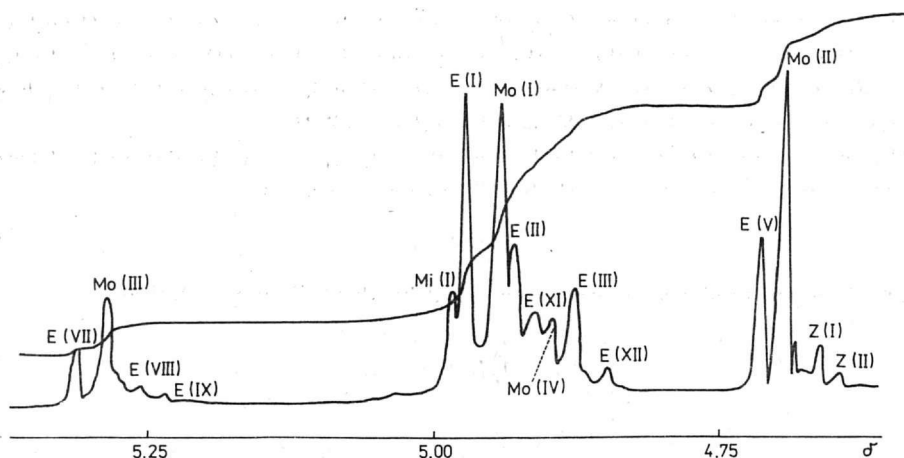
Fig. 3. ¹H-n.m.r. spectrum of water—methanol solution of formaldehyde with phenol. The number of moles of formaldehyde and methanol per 1 mole of phenol is 0.547 and 0.179, respectively.

δ_{12}—E(VII) end groups of polymer *III* C_6H_5O—CH_2—O— for $n = 2$

δ_{13}—Mo(III) phenoxymethanol C_6H_5O—CH_2—OH

δ_{14}—E(VIII) end groups of polymer *III* C_6H_5O—CH_2—O— for $n = 3$

δ_{15}—E(IX) end groups of polymer *III* C_6H_5O—CH_2—O— for $n > 3$

The protons of the methylene groups giving the earmarked signals are printed in italics. For calculation the intensity of signal of the methylene protons C_6H_5O—CH_2O—CH_2OH known from its ratio to E(VII) in the spectra of the system phenol—formaldehyde—water is taken into account. It was denoted E(X).

Simultaneously with the formation of polymer *III* a group of another three lines of polymer of the type $C_6H_5O(CH_2O)_n CH_3$ (*IV*) starts to appear on the right side of signal Mo. Since they are situated in the region of signals of polymers *I* and *II*, the determination of their intensities is difficult. Theoretical prerequisites of their formation are given by the presence of methanol in the system. Their appearance is made possible by phenol functioning as catalyst and their position may be theoretically assessed on the basis of the Shoolery effective constants of shielding. The signals were assigned as follows

δ_{16}—E(XI) C_6H_5O—CH_2O—CH_2O—CH_3

δ_{17}—Mo(IV) C_6H_5O—CH_2O—CH_3

δ_{18}—E(XII) C_6H_5O—CH_2O—CH_2O—CH_3

On the right side of signal Mo(II) two new signals of the protons of the methylene groups simultaneously arise from the molar ratio phenol : formaldehyde 1 : 2.2, too (Fig. 3). As these signals appear to the right from those of

methoxymethanol which closes from the right side the region of polymer *II* and it is known that the protons of the methylene groups of polymer *II* resonate in higher magnetic field, it may be assumed that the signals correspond just to these substances. They are denoted δ_{19}—Z(I) and δ_{20}—Z(II).

The molar concentration of hydroxymethanol, $c_{Mo(I)}$, may be determined from the total molar concentration of the CH_2O units in solution, c_0

$$c_{Mo(I)} = I_{Mo(I)} R \qquad (1)$$

where R is an auxiliary quantity expressed by the following relation

$$R = c_0 / \sum_{Mi=1}^{III} I_{Mi} + \sum_{E=1}^{XII} I_E + \sum_{Mo=1}^{IV} I_{Mo} + I_{Z(I)} + I_{Z(II)} \qquad (2)$$

The symbols $I_{Mi(I)}$ and $I_{Z(II)}$ stand for the intensities of signals of the protons of the —CH_2— groups expressed in terms of arbitrary units.

The molar concentration of methoxymethanol, $c_{Mo(II)}$, is given by the expression

$$c_{Mo(II)} = I_{Mo(II)} R \qquad (3)$$

Similarly the molar concentrations of phenoxymethanol, $c_{Mo(III)}$, and methoxyphenoxymethane, $c_{Mo(IV)}$, are given by the expressions

$$c_{Mo(III)} = I_{Mo(III)} R \qquad (4)$$

$$c_{Mo(IV)} = I_{Mo(IV)} R \qquad (5)$$

For the total molar concentration of all particles with CH_2O units, c, it may be written

$$c = \left[\sum_{Mo=1}^{IV} I_{Mo} + \left(\sum_{E=1}^{XII} I_E/2 \right) \right] R \qquad (6)$$

The molar concentrations of polymer *I* (c_1), polymer *II* (c_{II}), polymer *III* (c_{III}), and polymer *IV* (c_{IV}) are given by the following expressions

$$c_1 = [I_{Mo} + (I_{E(I)} + I_{E(II)}/2)] R \qquad (7)$$

$$c_{II} = [I_{Mo(II)} + (I_{E(III)} + I_{E(IV)} + I_{E(V)} + I_{E(VI)}/2)] R \qquad (8)$$

$$c_{III} = [I_{Mo(III)} + (I_{E(VII)} + I_{E(X)}/2)] R \qquad (9)$$

$$c_{IV} = [I_{Mo(IV)} + I_{E(XI)} + I_{E(XII)}/2)] R \qquad (10)$$

The relative proportion of hydroxymethanol (γ), methoxymethanol (γ'), phenoxymethanol (γ''), and phenoxymethoxymethanol (γ''') in the total mass of polymers *I*—*IV* may be calculated from the following expressions

Table 1

Characteristics of the system phenol—formaldehyde—water—methanol

Assignment	α^a	Number of moles of formaldehyde and methanol per 1 mole of phenol								
		29.182 / 9.635	14.591 / 4.818	7.296 / 2.409	4.387 / 1.433	2.189 / 0.717	1.094 / 0.358	0.547 / 0.179	0.369 / 0.119	0.219 / 0.072
c_0	13.260	12.770	12.319	11.514	10.590	8.820	6.611	4.405	3.309	2.201
$c_{Mo(I)}$	2.749	2.514	2.472	2.352	2.330	2.245	1.260	0.795	0.538	0.398
$c_{Mo(II)}$	1.294	2.321	2.410	2.475	2.330	1.764	1.339	0.856	0.620	0.426
$c_{Mo(III)}$	—	—	—	—	—	0.160	0.189	0.245	0.289	0.454
$c_{Mo(IV)}$	—	—	—	—	—	0.160	0.126	0.122	0.124	—
c	7.681	8.316	8.172	8.032	7.380	6.378	4.505	3.060	2.317	1.739
c_I	5.579	4.787	4.525	4.051	3.738	3.369	2.140	1.317	0.930	0.532
c_{II}	2.102	3.529	3.646	3.381	3.641	2.607	1.985	1.193	0.805	0.611
c_{III}	—	—	—	—	—	0.201	0.252	0.398	0.392	0.596
c_{IV}	—	—	—	—	—	0.201	0.189	0.168	0.186	—
γ	0.3579	0.3023	0.3024	0.2928	0.3158	0.2824	0.2795	0.2600	0.2326	0.2286
γ'	0.1684	0.2791	0.2949	0.3081	0.3158	0.2769	0.2961	0.2800	0.2680	0.2449
γ''	—	—	—	—	—	0.0252	0.0419	0.1000	0.1250	0.2612
γ'''	—	—	—	—	—	0.0252	0.0295	0.0400	0.0535	—
α_I	0.7002	0.5756	0.5538	0.5043	0.5066	0.5280	0.4750	0.4300	0.4020	0.3061
α_{II}	0.2998	0.4244	0.4462	0.4957	0.4934	0.4090	0.4400	0.3900	0.3480	0.3510
α_{III}	—	—	—	—	—	0.0315	0.0560	0.1300	0.1690	0.3429
α_{IV}	—	—	—	—	—	0.0315	0.0420	0.0549	0.0808	—

a) Aqueous methanolic solution of formaldehyde.

$$\gamma = \frac{c_{Mo(I)}}{c}, \qquad \gamma' = \frac{c_{Mo(II)}}{c}, \qquad \gamma'' = \frac{c_{Mo(III)}}{c}, \qquad \gamma''' = \frac{c_{Mo(IV)}}{c} \qquad (11\text{—}14)$$

The change in the ratio of individual components, *i.e.* polymers *I—IV* present in the system phenol—formaldehyde—water—methanol accompanying the change in the molar ratio of the above substances can be expressed by means of their relative proportions

$$\alpha_I = \frac{c_I}{c}, \qquad \alpha_{II} = \frac{c_{II}}{c}, \qquad \alpha_{III} = \frac{c_{III}}{c}, \qquad \alpha_{IV} = \frac{c_{IV}}{c} \qquad (15\text{—}18)$$

The results are summarized in Table 1.

It is also worth noticing that the approximate value obtained from the spectra with good resolution corresponding to the nearest higher and nearest lower concentration of phenol in the system phenol—formaldehyde—water—methanol was used as intensity for calculation if an overlapping of two signals occurred.

The accuracy of the results presented depends mainly on the method of evaluation of the relative intensities of signals in the spectra. The accuracy of the integrator the error of which is equal to 2% according to the information of producers ought also to be taken into account. The inaccuracy in the ratios of the starting mixture phenol—formaldehyde could be a source of errors, too.

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