

NMR STUDY OF WATER-METHANOL SOLUTIONS OF FORMALDEHYDE

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Equilibrium states of water-methanol solutions of formaldehyde were characterised by NMR spectra analysis. Formaldehyde concentration was 6.60 mol/l. The results presented here confirmed the former experimental knowledge about the effect of methanol added to water solution of formaldehyde on the degree of polycondensation, methylene glycol concentration *etc.*

By analyzing three lines of the NMR spectra of water solution of formaldehyde which represent $-\text{CH}_2-$ protons of polyoxymethylene glycols (inner groups Mi, end groups E, monomer Mo)^{1,2} the existence of hydrated form of formaldehyde and its prevalence over the nonhydrated form³ has been proved. The latter form is, however, not detectable by NMR spectroscopy as it follows from the experimental data obtained¹. Water-methanol solutions of formaldehyde are more complicated. In the first stage of the reaction of aliphatic alcohols with formaldehyde hemiacetals of the type of $\text{RO}(\text{CH}_2\text{O})_n\text{H}$ are formed. They are more stable than corresponding hydrates. Hemiacetals are in water-methanol solutions in an equilibrium with polyoxymethylene glycols⁴. In a neutral or an alkaline medium they are the only products of the reaction of formaldehyde with methanol. In an acidic medium the reaction proceeds further and gives acetals-formals and water:



EXPERIMENTAL

NMR spectra of water-methanol solutions of formaldehyde were run on a Tesla 487 A instrument at 80 MHz. Temperature of a sample was maintained at 80°C. Hexamethyldisiloxane (HMDS) in a sealed capillary was used as an external standard. The samples containing 6.60 mol/l of formaldehyde and variable amount of methanol were measured and evaluated. The results are summarized in Table I.

RESULTS AND DISCUSSION

The NMR spectra of water-methanol solutions of formaldehyde consist of seven individual signals (measured up to 20% wt. of formaldehyde) ranging from 4.6 to 5.0 τ (Fig. 1). Singlets of $-\text{CH}_2-$ protons of methylene glycol and that of polyoxymethylene glycol are identical with signals of solutions without methanol. New signals were assigned to protons of hemiacetals of the type $\text{CH}_3\text{O}(\text{CH}_2\text{O})_n\text{H}$.

A slight variation of chemical shifts of followed protons towards higher magnetic

field with increasing formaldehyde concentration in water-methanol solutions has been observed.

From the spectra comparison it follows: With increasing methanol concentration G_m (wt. %) and decreasing formaldehyde concentration G_{fd} (wt. %) the intensity of the seventh signal markedly increases. The singlets 4 and 6 are equally intensive, irrespective of formaldehyde and methanol concentrations. The substitution of hydrogen with methyl group shifts the signal towards higher magnetic field. Cyclic polymers are not present in the solutions in measurable quantities. Acetals are not formed in water-methanol solutions of formaldehyde at pH 4.0–4.5. The assignment of the NMR signals to the individual $-\text{CH}_2-$ groups with increasing magnetic field was done as follows:

- τ_1 : Mi inner groups $-\text{O}-\text{CH}_2-\text{O}-$ of polyoxymethylene glycols
 τ_2 : Mi' inner groups of hemiacetals of polyoxymethylene glycols $-\text{O}-\text{CH}_2-\text{O}-$
 τ_3 : E end groups of polyoxymethylene glycols $\text{HO}-\text{CH}_2-\text{O}-$
 τ_4 : E' end groups of hemiacetals of polyoxymethylene glycols $\text{HO}-\text{CH}_2-\text{O}-$
 τ_5 : Mo methylene glycol $\text{HO}-\text{CH}_2-\text{OH}$
 τ_6 : E'' $\text{CH}_3-\text{O}-\text{CH}_2-\text{O}-$ end groups of hemiacetals of polyoxymethylene glycols
 τ_7 : Mo' hemiacetal of formaldehyde and methanol $\text{CH}_3\text{O}-\text{CH}_2-\text{OH}$

TABLE I
Data of Water-Methanol Solutions of Formaldehyde

Sample	1	2	3	4	5	6
G_{fd}	18.70	20.0	20.3	20.8	21.4	21.8
G_m	0	5.43	11.0	19.1	27.2	41.3
c_0	6.60	6.60	6.60	6.60	6.60	6.60
n_1^x	2.80	3.25	3.65	4.31	5.02	5.49
n_1	2.80	2.51	2.33	1.74	1.20	0.47
n_1'	—	0.68	1.32	2.50	3.67	5.02
y	4.41	4.69	4.96	5.32	5.70	6.02
y_g	4.41	3.79	3.27	2.45	1.46	0.53
y_p	—	0.88	1.96	2.87	4.28	5.49
γ_1^x	0.635	0.683	0.735	0.802	0.875	0.911
γ_1	0.635	0.556	0.470	0.442	0.209	0.078
γ_1'	—	0.135	0.265	0.338	0.666	0.833
\overline{M}	62.8	62.7	62.7	62.8	63.1	63.8
\overline{M}_g	62.8	60.3	58.7	56.9	54.1	51.3
\overline{M}_p	—	71.8	70.2	68.0	66.1	62.6

The contribution of inner groups of hemiacetals having number of CH_2O groups higher than 3 could be included in the signal Mi. Similarly, the contribution of the end groups $\text{HO}-\text{CH}_2-$ of hemiacetals of polyoxymethylene glycols having the number of CH_2O groups higher than 3 would add to the signal E. But this does not seem to be the case as the intensity ratio of the fourth and the sixth signal is constant up to formaldehyde concentration of 37%. However, the fact is that the signal E splits and that the split widens with increasing both methanol and formaldehyde concentrations. As it follows from the spectra, the contribution of $-\text{CH}_2\text{O}-$ groups of polymers having the number of units higher than 3 is, in the concentration range used, lower than 5%. Therefore the error arising from such a spectra evaluation cannot substantially affect the characterization of solution equilibrium states.

Knowing the molar formaldehyde concentration in water-methanol solution (c_0), the total molar concentration of monomer n_1^x can be calculated from the following equation

$$n_1^x = (p_{M_0} + p_{M_0'}) \cdot R, \quad (2)$$

where

$$R = c_0 / (p_{M_0} + p_{M_0'} + p_{M_i} + p_{M_i'} + p_E + p_{E'} + p_{E''}), \quad (3)$$

p_{M_i} ; $p_{M_i'}$; p_E ; $p_{E'}$; $p_{E''}$; p_{M_0} ; $p_{M_0'}$ are the signal intensities of $-\text{CH}_2-$ protons in arbitrary units.

From the value of n_1^x , which includes molar concentration of methylene glycol and molar concentration of formaldehyde-methanol hemiacetal (n_1 and n_1'), it is possible to calculate both concentrations according to

$$n_1 = p_{M_0} \cdot R, \quad (4)$$

$$n_1' = p_{M_0'} \cdot R. \quad (5)$$

Total concentration of all components is:

$$y = [p_{M_0} + p_{M_0'} + (p_E + p_{E'} + p_{E''})/2] \cdot R. \quad (6)$$

In a similar way it is possible to calculate total molar concentration of components of polyoxymethylene glycols y_g and of hemiacetals of polyoxymethylene glycols y_p .

$$y_g = [p_{M_0} + (p_E/2)] \cdot R, \quad (7)$$

$$y_p = [p_{M_0'} + (p_{E'} + p_{E''})/2] \cdot R. \quad (8)$$

However, the calculations of y_g and y_p can be erroneous due to the contribution of

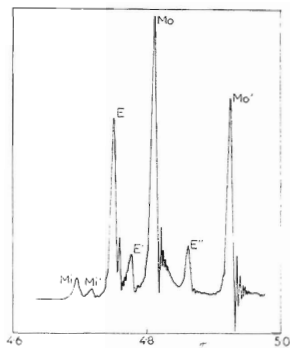


FIG. 1
 ^1H NMR Spectrum of Water-Methanol
 Solutions of Formaldehyde
 20% wt. of formaldehyde, 11% wt. of
 methanol.

— CH_2O — groups of polyoxymethylene hemiacetals having higher degree of polymerization.

The total monomer ratio is given by

$$\gamma_1^x = n_1^x/y. \quad (9)$$

Therefore, the methylene glycol and the formaldehyde-methanol hemiacetal ratios can be expressed as

$$\gamma_1 = n_1/y, \quad \gamma_1' = n_1'/y. \quad (10, 11)$$

The total average molecular weight is then given by

$$\bar{M} = \frac{48p_{\text{Mo}} + 62p_{\text{Mo}'} + 30(p_{\text{Mi}} + p_{\text{Mi}'}) + 39(p_{\text{E}} + p_{\text{E}'}) + 53p_{\text{E}''}}{(p_{\text{E}} + p_{\text{E}'} + p_{\text{E}''})/2 + p_{\text{Mo}} + p_{\text{Mo}'}} \quad (12)$$

and the average molecular weight of polyoxymethylene glycols can be expressed as

$$\bar{M}_n = (48p_{\text{Mo}} + 30p_{\text{Mi}} + 39p_{\text{E}})/(p_{\text{E}}/2 + p_{\text{Mo}}) \quad (13)$$

and the average molecular weight of hemiacetals of polyoxymethylene glycols is the following

$$\bar{M}_p = (62p_{\text{Mo}'} + 30p_{\text{Mi}'} + 39p_{\text{E}'} + 53p_{\text{E}''})/[(p_{\text{E}'} + p_{\text{E}''})/2 + p_{\text{Mo}'}]. \quad (14)$$

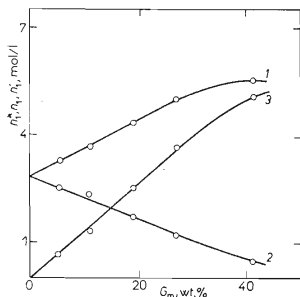


FIG. 2

Molar Monomer Concentration vs Methanol Concentration in Water-Methanol Solution of Formaldehyde

1 n_1^x ; 2 n_1 ; 3 n_1' .

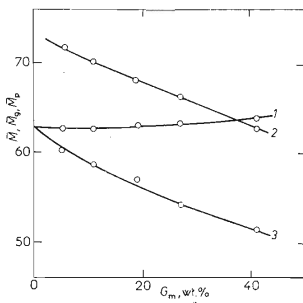


FIG. 3

Effect of Methanol Concentration in Water-Methanol Solution of Formaldehyde on Weight-Average Molecular Weight

1 \bar{M} ; 2 \bar{M}_g ; 3 \bar{M}_p .

$$M_{M_0} = 48 \text{ for } \text{CH}_2(\text{OH})_2$$

$$M_{M_0'} = 62 \text{ for } \text{CH}_3\text{OCH}_2\text{OH}$$

$$M_{E,E'} = 39 \text{ for } \text{HO}-\text{CH}_2-\text{O}-,$$

$$M_{E''} = 53 \text{ for } \text{CH}_3-\text{O}-\text{CH}_2-\text{O}-,$$

$$M_{M_i, M_i'} = 30 \text{ for } -\text{O}-\text{CH}_2-\text{O}-.$$

All samples measured were evaluated with the use of preceding equations. Graphical representation of the results is given in Figs 2 and 3. The increase of the average molecular weight \bar{M} with increasing methanol concentration in water-methanol solution of formaldehyde given in Fig. 3 is purely relative, as at low formaldehyde concentrations the concentration of monomers in the solution can be as high as 70%. Therefore the difference in molecular weights of methylene glycol (48) and of formaldehyde-methanol hemiacetal (62) strongly affects the value of \bar{M} . The error of \bar{M} determination is given mainly by the error of the spectrometer integrator and is in the region of $\pm 1\%$.

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