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Association of Formaldehyde in Aqueous-Alcoholic Systems

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Abstract—In the neutral systems formaldehyde–water–alcohol (methanol, ethanol, ethylene glycol) at 25°C, formaldehyde is preferentially present as hemiacetals. The mean equilibrium constants of step polycondensation of formaldehyde are calculated.

Dissolution of formaldehyde in water results in formation in the solutions of equilibrium mixtures of monomeric formaldehyde and polyoxymethylene glycols $HO(CH_2O)_nH$ [1–4] [Eqs. (1)–(3)].

$$CH_2O + H_2O \rightleftarrows HOCH_2OH, \qquad (1)$$

$$HOCH_2OH + HOCH_2OH \rightleftarrows HO(CH_2O)_2H + H_2O, \qquad (2)$$

$$H(OCH_2)_nOH + HOCH_2OH \rightleftarrows H(OCH_2)_{n+1}OH + H_2O. \qquad (3)$$

Solutions of formaldehyde in alcohols are equilibrium mixtures of monomeric formaldehyde and hemiacetals $RO(CH_2O)_nH$ [1, 5–7] [Eqs. (4)–(6)]:

$$CH_2O + RCH_2OH \overset{K_1}{\rightleftarrows} HOCH_2OCH_2R, \qquad (4)$$

$$HOCH_2OCH_2R + HOCH_2OCH_2R \overset{K_2}{\rightleftarrows} H(OCH_2)_2OCH_2R + RCH_2OH, \qquad (5)$$

$$N(OCH_2)_mOCH_2R + HOCH_2OCH_2R \overset{K_N}{\rightleftarrows} H(OCH_2)_{m+1}OCH_2R + RCH_2OH. \qquad (6)$$

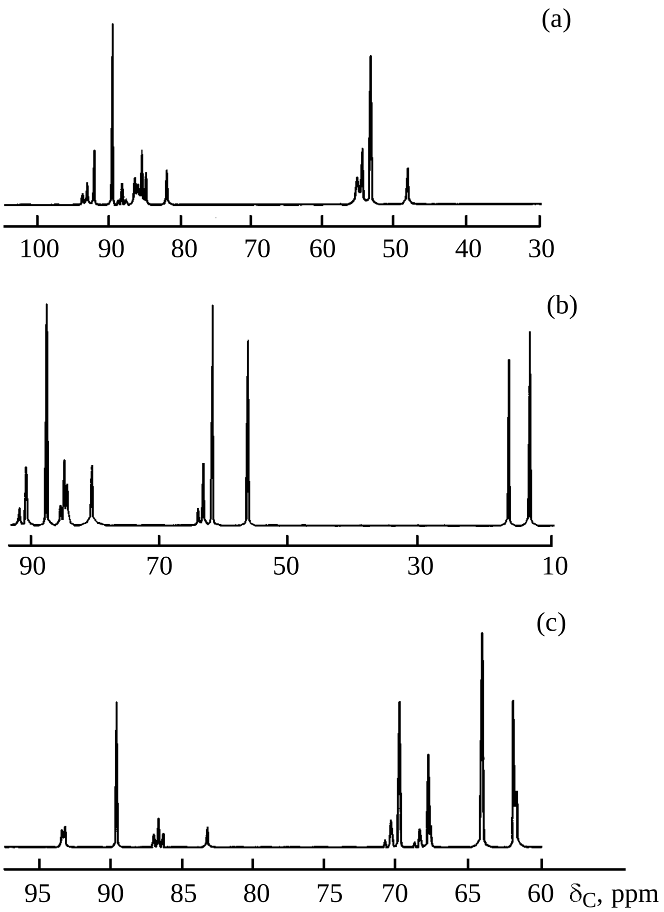
Solutions of formaldehyde in ethylene glycol contain two types of hemiacetals: $H(OCH_2)_nOCH_2 \cdot CH_2OH$ (type A) and $H(OCH_2)_mOCH_2CH_2O(CH_2O)_kH$ (type B) [5, 8].

Addition of methanol to aqueous solutions of formaldehyde results not only in reaction between formaldehyde and methanol, but also shifts equilibria (1)–(3) to lower oligomers [1, 9–12]. Therewith, the shifts are the stronger the more methanol is added. This effect explains the use of methanol for stabilization of Formalin. Quantitative studies on the equilibrium in the formaldehyde–water–methanol system [12] showed that formaldehyde in this ternary system reacts with water and methanol concurrently and independently. However, there is lack of data in the literature concerning the effect of the composition of the water–alcohol system on the molecular-weight distribution of polyoxymethylene glycols and hemiacetals.

The aim of the present work was to study the composition of the equibrium mixtures of associates of formaldehyde dissolved in water–methanol, water–ethanol, and water–ethylene glycol mixtures at 25°C. For the instrumental method we used ^{13}C NMR, since it provides reliable qualitative and quantitative information on the molecular-weight distiributions of formaldehyde associates of various types [2–5, 8, 13, 14]. The spectra of the solutions were assigned based on the spectra of individual alcohols [13], glycol [8], and solutions of formaldehyde in water [2–4] and ethylene glycol [8], as well as from the dependences of the spectral patterns on the concentrations of the components and known chemical shift–structure relationships [2–4, 13, 14].

The ^{13}C NMR spectra of solutions of formaldehyde in water–methanol, water–ethanol, and water–ethylene glycol mixtures (see Figs. 1a–1c, respectively) characteristically display a group of signals at δ_C 80–95 ppm, which were assigned to hydroxymethylene CH_2 groups of polyoxymethylene glycols and hemiacetals. We failed to assign signals inside these groups, and, therefore, as earlier, most information on the qualitative and quantitative compositions of the equilibrium mixtures was gained from an analysis of signals belonging to alcoholic fragments.

In the spectra of the formaldehyde–water–methanol system, the CH_3 groups of methanol and hemiacetals appear at δ_C 45–55 ppm. Analyzing the spectra of the mixture, one can note that replacement of OH by OCH_2OH shifts the signal downfield by ~5.2 ppm (Table 1), while replacement of OH by $OCH_2 \cdot OCH_2OH$ shifts the signal downfield by ~5.8 ppm. In addition, in the above spectral range there is one more



^{13}C NMR spectrum of solutions of formaldehyde in water–alcohol mixtures. (a) c_{HCHO} 12.92, c_{MeOH} 10.15, and c_{H_2O} 16.52 M; (b) c_{HCHO} 8.126, c_{EtOH} 9.13, and c_{H_2O} 15.87 M; and (c) c_{HCHO} 9.107, $c_{(CH_2OH)_2}$ 10.29, and c_{H_2O} 10.73 M.

signal at δ_C 54.67 ppm, which we assigned to hemiacetals of the general formula $CH_3O(CH_2O)_nH$ ($n \geq 3$).

In the spectrum of the formaldehyde–water–ethanol system, there are two groups of signals from the CH_3 groups of the alcoholic fragments of the alcohol and hemiacetals: δ_C 10–20 and 55–65 ppm. Replacement in ethanol of the OH group by oxymethylene chains shifts the CH_3 signal upfield and the CH_2 signal, downfield; therewith, the CH_2 signal is more sensitive to the length of the oxymethylene chain, and, therefore, the component concentrations were calculated based on the intensities of the alcoholic CH_2 signals. Replacement of OH by OCH_2OH shifts the signal downfield by ~5.6 ppm (Table 1).

Replacement of OH by OCH_2OCH_2OH shifts the signal downfield by ~6.4 ppm. The alcoholic CH_2 group of hemiacetals of the general formula $CH_3CH_2 \cdot O(CH_2O)_nH$ ($n \geq 3$) gives a single signal (δ_C 63.34 ppm).

The assignment of alcoholic group signals of the formaldehyde–water–ethylene glycol is the same as in [8].

The spectra of the formaldehyde–alcohol systems obtained by barboting gaseous formaldehyde through the column of the alcohol (Tables 2 and 3, exp. nos. 1, 5, and 9) and containing small amounts of water (~0.1–1 M) show no methylene glycol $HOCH_2OH$ signal, implying lack of polyoxymethylene glycols in these systems. As the concentration of water is increased to 16–18 M (1.5–2-fold molar excess of water with respect to alcohol and formaldehyde), a methylene glycol signal appears in the spectra of the ternary systems. The fraction of the intensity of the methylene glycol signal in the total

Table 1. Assignment of signals in the ^{13}C NMR spectra of the formaldehyde–water–alcohol systems

Signal no.	δ_C, ppm	Assignment	Correction factor
		Formaldehyde–water–methanol	
1	48.45	CH_3OH	1.209
2	53.62	$HOCH_2OCH_3$	0.989
3	54.29	$HOCH_2OCH_2OCH_3$	0.948
4	54.67	$H(OCH_2)_nOCH_3$, $n \geq 3$	0.927
5	81.84	$HOCH_2OH$	1.073
		Formaldehyde–water–ethanol	
1	13.87	$CH_3CH_2O(CH_2O)_nH$, $n \geq 2$	–
2	13.93	$CH_3CH_2OCH_2OH$	–
3	16.76	CH_3CH_2OH	–
4	56.62	CH_3CH_2OH	1.045
5	62.23	$CH_3CH_2OCH_2OH$	1.064
6	63.01	$CH_3CH_2O(CH_2O)_2H$	0.870
7	63.34	$CH_3CH_2O(CH_2O)_nH$, $n \geq 3$	0.521
8	81.46	$HOCH_2OH$	1.306
		Formaldehyde–water–ethylene glycol	
1	60.19	$HOCH_2CH_2O(CH_2O)_nH$, $n \geq 2$	–
2	60.33	$HOCH_2CH_2OCH_2OH$	0.978
3	62.28	$HOCH_2CH_2OH$	1.044
4	65.88	$HOCH_2OCH_2CH_2O(CH_2O)_2H$	–
5	66.03	$HOCH_2OCH_2CH_2OCH_2OH$	0.948
6	66.46	$H(OCH_2)_2OCH_2CH_2O(CH_2O)_2H$ $HOCH_2OCH_2CH_2O(CH_2O)_2H$	0.879
7	68.28	$HOCH_2CH_2OCH_2OH$	1.000
8	68.74	$HOCH_2CH_2OCH_2OCH_2OH$	0.931
9	68.91	$HOCH_2CH_2O(CH_2O)_3H$	–
10	81.58	$HOCH_2OH$	0.898

Table 2. Equilibrium compositions of solutions of formaldehyde in alcohol–water mixtures (*c*, M)

Exp. no.	Total concentration			$[ROH]_{free}$	$[RO(CH_2O)_nH]$			$[HOCH_2OH]$
	HCHO	ROH	water		$n = 1$	$n = 2$	$n \geq 3$	
				R = Me				
1	18.30	14.30	0.1177	2.688	6.594	3.349	1.669	—
2	16.57	13.02	5.591	2.474	6.344	2.616	1.586	0.2365
3	15.16	11.90	11.85	2.059	6.380	2.224	1.237	0.6165
4	12.92	10.15	16.52	1.591	5.859	1.873	0.8266	0.8359
				R = Et				
5	11.23	12.57	0.1428	4.139	6.071	1.927	0.4331	—
6	10.19	11.46	5.234	3.780	5.851	1.455	0.3737	0.3074
7	9.164	10.30	10.42	3.495	5.285	1.238	0.2823	0.5564
8	8.126	9.130	15.87	3.395	4.394	1.063	0.2783	0.7703

Table 3. Equilibrium compositions of solutions of formaldehyde in ethylene glycol–water mixtures (*c*, M)

Exp. no.	Total concentrations			c_{eg}^{free}	c_A				c_B			c_{mg}
	HCHO	$(CH_2OH)_2$	water		$n = 1$	$n = 2$	$n = 3$	$n > 3$	$m = 1,$ $k = 1$	$m = 1,$ $k = 2$	$m \geq 2,$ $k \geq 2$	
9	13.50	12.08	1.108	1.957	3.140	1.172	0.8323	0.4554	1.733	1.425	1.326	–
10	11.55	10.60	6.230	2.991	4.542	0.9160	0.2422	–	1.273	0.6357	–	0.1794
11	9.996	9.364	12.22	2.922	3.906	0.7464	0.1616	–	1.137	0.4912	–	0.3572
12	8.934	8.180	18.11	2.487	3.535	0.6183	0.1499	–	0.9848	0.4051	–	0.5037
13	9.107	10.29	10.73	3.878	4.277	0.7121	–	–	1.055	0.3684	–	0.3042
14	6.245	12.60	7.362	7.492	4.196	0.3893	–	–	0.5216	–	–	0.1732
15	3.634	14.64	4.282	11.20	3.250	–	–	–	0.1921	–	–	–
16	1.997	15.81	2.353	13.81	1.997	–	–	–	–	–	–	–

intensity of the oxymethylene signal of polyoxymethylene glycols and hemiacetals was 0–6.5% for methanol, 0–9.5% for ethanol, and 0–5.6% for ethylene glycol (Tables 2, 3). Since increasing water concentration gave no rise to new signals near δ_C 80–95 ppm, in concentration calculations were supposed that the formaldehyde–water–alcohol systems contain no other formaldehyde hydration and condensation products [reactions (1)–(3)] than methylene glycol.

The component concentrations calculated from the corresponding signal areas are listed in Tables 2 and 3. These data can be used to calculate the step formaldehyde polycondensation equilibrium constants for aliphatic alcohols (K_N).

$$K_N = ([RO(CH_2O)_{n+1}H]\,[ROH]_{free})/([RO(CH_2O)_nH] \cdot [ROCH_2OH]).$$

The resulting mean step formaldehyde polycondensation equilibrium constants for methanol and ethanol are listed below.

	K_2	K_3
MeOH	0.1418 ± 0.0532	0.1847 ± 0.0492
EtOH	0.1797 ± 0.0281	0.1681 ± 0.0238

The quantitative and qualitative composition of the equilibrium mixture in the formaldehyde–water–ethylene glycol system is determined by step polycondensation equilibrium constants $K_{m,k}$.

$$H(OCH_2)_mOCH_2CH_2O(CH_2O)_kH + HOCH_2CH_2OCH_2OH \xrightleftharpoons{K_{m,k}} H(OCH_2)_{m+1}OCH_2CH_2O(CH_2O)_kH + HOCH_2CH_2OH.$$

The calculated mean formaldehyde polycondensation equilibrium constants for ethylene glycol are as follows: K_{02} 0.1580 ± 0.0394, K_{03} 0.2373 ± 0.1369, K_{11} 0.2274 ± 0.0534, and K_{12} 0.3541 ± 0.0898.

The resulting step formaldehyde polycondensation equilibrium constants for the same alcohols in the absence of water fairly agree with data in [5, 8]. We can thus conclude that in equilibrium formaldehyde–water–alcohol (methanol, ethanol, ethylene glycol) systems in our experimental conditions formaldehyde is almost completely bound into hemiacetals, and water is present, within experimental error, as an inert solvent. These conclusions are consistent with data in [12] for the formaldehyde–water–methanol system.

Introduction into the neutral mixture formaldehyde–water–alcohol of an acid catalyst would favor accumulation of acetals in the system [15, 16]. Such process, in particular, forms the basis of the industrial production of 1,3-dioxolane by the reaction of formaldehyde with ethylene glycol. For constructing a mathematical model of the process, one should know the ratio of polyoxymethylene glycols and hemiacetals in the reaction mixtures. Table 3 lists (exp. nos. 13–16) the molecular-weight distribution of components of formaldehyde–water–ethylene glycol mixtures at varied glycol:formaldehyde molar ratio (from ~1 to ~8). These data show that in the above mixtures formaldehyde is mostly present as a monosubstituted hemiacetal of type A, and, therewith, formaldehyde is almost completely bound into hemiacetals.

EXPERIMENTAL

The ^{13}C NMR spectra were measured at 25°C on a Varian Gemini-300 Fourier spectrometer at 75 MHz. For stabilization of resonance conditions, a thin ampule with $(CD_3)_2SO$ was inserted into the ampule with the sample; the signal of $(CD_3)_2SO$ was also used as reference (δ_C 39.49 ppm). The proportionality between signal intensities and the number of absorbing nuclei [13], was provided by using correction factors [8, 14]. The concentrations were determined with an accuracy of no worse than ±5 rel.%.

Aqueous and alcoholic solutions of formaldehyde were prepared by barboting through the corresponding solvent gaseous formaldehyde obtained by decomposition of Paraform in a glass reactor at 130–150°C. Aqueous-alcoholic solutions of formaldehyde were prepared by diluting binary mixtures with the corresponding solvent. The resulting mixtures were left to stand at 25°C for no less than 24 h before use. Analysis of the mixtures for formaldehyde was performed by the sulfite procedure [1]. Analysis of the mixtures for water was performed according to Fischer.

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