# Solubilization of Nitrogen-Containing Heterocyclic Compounds in Reactive Solvents

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**ABSTRACT:** A reactive solvent was obtained by reacting 1 mol of cyclohexanone with 5 mol of formaldehyde. The structure of the solvent was studied by using $^1$H-NMR and IR spectroscopy. It was used for solubilization of melamine and other heterocyclic compounds containing —NH— groups, such as adenine, carbazole, cytozine, guanine, thymine, and uracyl, as well as isocyanuric, barbituric, and uric acids. The solubilization involved the reaction of formaldehyde (liberated at an elevated temperature) with amino groups of the compound. Melamine was the compound with the best solubility in the reactive solvent. Preliminary attempts of curing the solutions have also been made. The oligomers cured at 120°C in the presence of acidic catalysts. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 2650–2659, 2002

**Key words:** solution properties; heteroatom-containing polymers; structure–property relations

## INTRODUCTION

1,3,5-triazine-2,4,6-triamine, known as melamine, is an important heterocyclic compound widely used in the polymer industry in the production of melamine–formaldehyde resins. The presence of *s*-triazine ring in the melamine molecule furnishes the polymers obtained from it with relatively high thermal stability and good dielectric properties.[1]

The main disadvantage of melamine is its poor solubility in organic solvents. Anhydrous solvents for melamine that would allow more extensive applications of this compound and its derived polymers have been sought for many years.[2]

Following Wirpsza,[3] we have applied as reactive solvents the hydroxymethyl derivatives of ketones, aldehydes and other compounds having C—H link activated by a vicinal carbonyl group. In basic medium these compounds easily react with formaldehyde according to the scheme:[3]



$$(1)$$
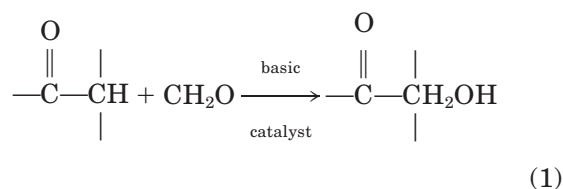
By dissolving melamine in reactive solvents of this kind, and subsequently processing the solution, new polymers were obtained, which differed from the classical melamine–formaldehyde resins.[4] Melamine has been found to dissolve not only physically; it also reacted with the solvent, yielding a resinous reactive system. At elevated temperatures and in either acidic or basic medium, the system further reacted and eventually gelled and hardened.

The dissolution consisted of the following reactions:

- dissociation of formaldehyde from $O$-hydroxymethyl groups of the reactive solvent:

$$\begin{array}{c} \mathrm{O} \\ \parallel \\ -\mathrm{C}-\mathrm{CH}-\mathrm{CH_2}-\mathrm{O}-\mathrm{CH_2OH} \;\rightleftharpoons \\ | \\ \\ \mathrm{O} \\ \parallel \\ -\mathrm{C}-\mathrm{CH}-\mathrm{CH_2}-\mathrm{OH} + \mathrm{CH_2O} \quad (2) \\ | \end{array}$$
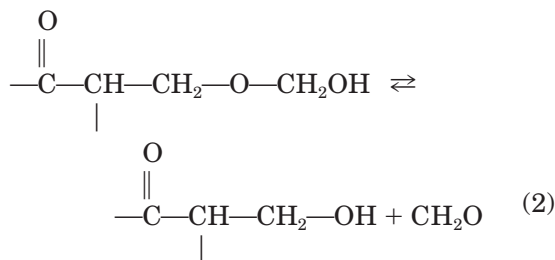
- addition of a —$NH_2$ group of melamine or other compound to formaldehyde to yield a $N$-hydroxymethyl group:

$$-\mathrm{NH_2} + \mathrm{CH_2O} \rightleftharpoons -\mathrm{NH}-\mathrm{CH_2}-\mathrm{OH} \quad (3)$$

- condensation of hydroxymethyl groups of melamine with those of reactive solvents[2]:

$$\begin{array}{c} \mathrm{O} \\ \parallel \\ -\mathrm{NH}-\mathrm{CH_2}-\mathrm{OH} + \mathrm{HO}-\mathrm{CH_2}-\mathrm{CH}-\mathrm{C}- \;\rightarrow \\ | \\ \\ \mathrm{O} \\ \parallel \\ -\mathrm{NH}-\mathrm{CH_2}-\mathrm{O}-\mathrm{CH_2}-\mathrm{CH}-\mathrm{C}- + \mathrm{H_2O} \\ | \end{array}$$

$$(4)$$
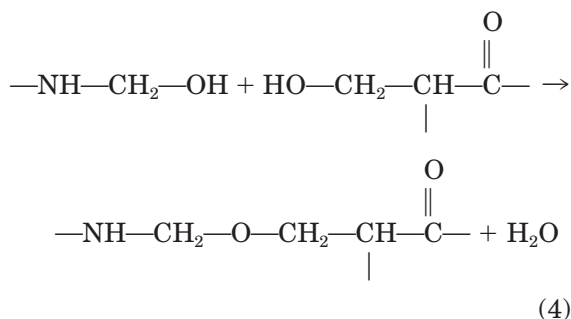
or:

- condensation of amino (amide) groups with polyoxymethylene groups of the reactive solvent[2]:

$$\begin{array}{c} \mathrm{O} \\ \parallel \\ -\mathrm{NH_2} + \mathrm{HO}-\mathrm{CH_2}-\mathrm{O}-\mathrm{CH_2}-\mathrm{CH}-\mathrm{C}- \;\rightarrow \\ | \\ \\ \mathrm{O} \\ \parallel \\ -\mathrm{NH}-\mathrm{CH_2}-\mathrm{O}-\mathrm{CH_2}-\mathrm{CH}-\mathrm{C}- + \mathrm{H_2O} \\ | \end{array}$$

$$(5)$$
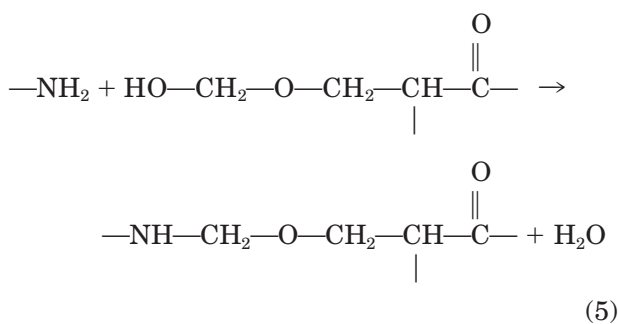
Other heterocyclic compounds with amine (or amide) groups that are hardly soluble in organic solvents (Table I)[5–9] could be expected to behave similarly to melamine, obtaining a new group of condensation polymers with heteroatom-containing rings.

## EXPERIMENTAL

### Synthesis of Adduct Containing 1 mol of Cyclohexanone and 5 mol of Formaldehyde (5-HMCH)

Into a round-bottomed 250 cm$^3$ flask equipped with a reflux condenser, thermometer and mechanical stirrer, 34.3 g (0.35 mol) of cyclohexanone and 153.8 g of formalin (34.8% 1.75 mol) of formaldehyde were placed. Triethylamine was then added in the amount sufficient to raise the pH to 11 (about 0.7 cm$^3$). The reaction was carried out at 80°C for 5.5 h. From a small reactor where simultaneous reaction was carried out, 1 cm$^3$ samples were withdrawn and the content of formaldehyde determined.[10] The analysis was continued until equilibrium was reached in the system. The reaction was then considered to be completed. The excess water was distilled off under reduced pressure ($p = 920 \div 1400$ Pa), while keeping the mixture temperature below 50°C. The molar ratio of cyclohexanone to formaldehyde (calculated from mass balance) was also confirmed by $^1$H-NMR.

### Chemical and Spectral Analyses

#### Formaldehyde Determination

The reaction of cyclohexanone with formalin was followed by determining free formaldehyde content by using the sulfite method.[10]

#### Spectral Analyses

Infra-red analysis were made by using the horizontal ATR technique on a PARAGON 1000 FT spectrometer (Perkin Elmer). The samples were capillary films. $^1$H-NMR spectra were recorded on a TESLA BS-587A spectrometer (80 MHz) in d$_6$-DMSO with hexamethyldisiloxane as internal standard.

#### The Mass Balance

The mass balance of the reaction between 1 mol of cyclohexanone with 5 mol of formaldehyde (5-HMCH synthesis) was made by weighing (to accuracy 0.1 g)

**Table I  Solubility of Nitrogen-Containing Heterocyclic Compounds**

| Heterocyclic Compound | Solubility[a] (g/100 g solvent) | | | | | | | Acids | | | Bases | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Water | Ethyl Alcohol | Ethyl Ether | Aceton | Benzene | DMF | DMSO | HCl | $H_2SO_4$ | $HNO_3$ | $NH_{3\ 25\%aq}$ | $NaOH_{50\%aq}$ |
| Mel | $0.32^{20°C}$ $5.2^{100°C}$ | 4.0 in glycol 11.0 in glycerine | $0.9^{30°C}$ $1.1^{90°C}$ | I | I | I | S | I | I | I | $3.6^{0°C}$ $2.4^{100°C}$ | S |
| CA | $0.2^{25°C}$ $0.75^{0°C}$ $2.6^{90°C}$ | $0.1^{21°C}$ | I | I | $0.23^{25°C}$ | $6.7^{25°C}$ | $15.1^{25°C}$ | I | S | I | S | S |
| BA | S | I | I | I | I | S | S | S | I | S | S | S |
| UA | $0.002^{0°C}$ $0.009^{30°C}$ $0.625^{100°C}$ | I | I | I | I | S | S | I | S | I | S | S |
| Ade | $0.09^{15°C}$ $2.50^{100°C}$ | S | I | I | I | I | S | I | S | S | S | S |
| Gua | $0.004^{40°C}$ | S | I | I | I | I | I | I | S | S | S | S |
| Car | I | $0.92^{14°C}$ $3.88^{78°C}$ | $2.5^{16°C}$ | $11.0^{30°C}$ | $0.7^{16°C}$ $5.0^{50°C}$ | S | S | I | I | I | I | I |
| Cyt | $0.87^{25°C}$ | S | I | I | S | S | S | S | S | S | S | S |
| Thy | $0.74^{22°C}$ | S | I | I | I | S | S | S | S | S | S | S |
| Ura | S cold S hot | I | I | I | I | S | S | S | S | S | S | S |

Compounds in selected solvents.[5–9]

[a] S = soluble; I = insoluble; S = slightly soluble.

- substrates
- the post-reaction mixture
- the product after water and catalyst had been distilled off.

### *Properties of the Reactive Solvent*

The hydroxymethyl derivative of cyclohexanone (after removing water under reduced pressure) was characterized by measuring the refractive index at 20°C with an Abbe Refractometer, the density in a pycnometer, the viscosity with a Höppler Viscometer, and the free formaldehyde content by the sulfite method.

### **Solubility of Heterocyclic Compounds in Reactive Solvent**

### *With Gradual Compound Introduction*

3 g of reactive solvent (RS) was placed in a 25 cm$^3$ beaker and the heterocyclic compound (HC) was introduced in $\cong$0.1 g portions. The mixture was heated and stirred with thermometer until the compound dissolved. The temperature was recorded (90–120°C). The next portion was introduced only after the previous one has dissolved. The procedure was stopped when the mixture started to thicken and gel or when the next portion failed to dissolve.

### *With One-Step Introduction of the Compound*

A sample of heterocyclic compound of the size determined by the gradual introduction method was dissolved in 3 g of RS at the temperature $\cong$10°C below that when the system quickly gels (Table II). Further amounts of the compound were again added to the solution obtained in 0.1 g portions. From the resulting clear solution a droplet was withdrawn and cooled to room temperature. The procedure was continued until the withdrawn solution no longer became clouded. This tested whether or not the heterocycle with RS would form a homogeneous system at room temperature.

### *With Extra 10–40 wt % of Water*

A sample of heterocyclic compound of the size determined by the single introduction method was dissolved in 3 g of RS and 10 wt % of water was added. After dissolution, further 0.1 g portions of the compound were added. The procedure was halted when the system started to thicken

and gel. Further dissolution experiments were continued each time by increasing the amount of water by 5 wt % until the total content of water in the RS was 40 wt %. In each RS–water system the amount of heterocyclic compound was determined independently. Attempts at which the amount of solute determined in the preceding experiment (with less water) was introduced at once were also carried out.

The solubilities presented in Table II are expressed in grams of solute dissolved in 100 g of solution (per final mass), $R_{HC}$. In the experiments with temperature exceeding 100°C, some part of volatile components (water, formaldehyde) evaporated and the total mass of the final solution was smaller than the sum of mass of all introduced components. The final percentage of the solute in the system is also presented in Table II.

### **Attempts at Curing the Solutions of Heterocyclic Compounds**

To the solution of a heterocyclic compound (HC) in RS, 0.5, 1.0, or 2.0 wt % of concentrated hydrochloric (36%), formic (80%), or acetic acid (80%) were introduced gradually, while keeping the temperature below that of dissolution. The solvents were heated at 100°C until gelled. Gelling experiments were also carried out by placing the solution with a catalyst on a glass plate and heating them at 120°C for 20–180 min (Table III).

## RESULTS AND DISCUSSION

The reactive solvent for heterocyclic compounds was obtained in reactions of cyclohexanone with formaldehyde (introduced as formalin) at 80°C and in the presence of triethylamine catalyst:

$$\begin{array}{c} O \\ \parallel \\ -C-CH_2- \end{array} + 2CH_2O \rightarrow$$

$$\begin{array}{c} O \\ \parallel \\ -C-C \end{array} \diagup \begin{array}{c} CH_2OH \\ \diagdown CH_2OH \end{array} \xrightarrow{n\ CH_2O} \begin{array}{c} O \\ \parallel \\ -C-C \end{array} \diagup \begin{array}{c} (CH_2O)_xH \\ \diagdown (CH_2O)_yH \end{array}$$

$$(6)$$
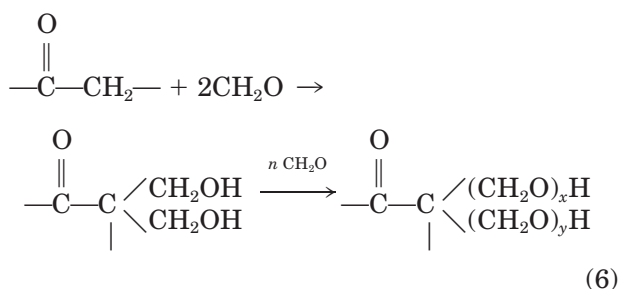
with $x + y = n + 2$.

The end of the reaction was determined by following the concentration of formaldehyde. The

**Table II  Solubilities of Nitrogen-Containing Heterocyclic Compounds (HC)[a]**

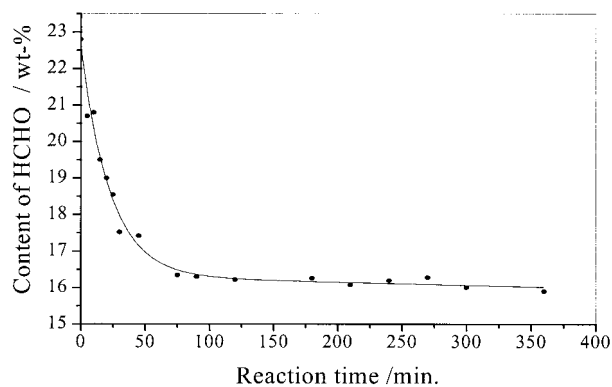| Heterocyclic Compound | Water Added (wt %) | Solubility $(R_{HC})$[b] | Concentration of Heterocyclic Compound in RS (wt %) |
|---|---|---|---|
| Melamine | 0 | 26.1 | 22.1 |
| | 10 | 38.8 | 29.9 |
| | 15 | 56.0 | 36.6 |
| | 20 | 69.8 | 41.1 |
| | 25 | 76.3 | 43.3 |
| | 30 | 79.9 | 44.5 |
| | 35 | 88.7 | 47.0 |
| | 40 | 92.8 | 47.6 |
| Isocyjanuric Acid | 0 | 45.0 | 36.3 |
| | 5 | 49.7 | 37.4 |
| | 10 | 56.1 | 37.5 |
| | 15 | 55.1 | 35.5 |
| | 20 | 54.4 | 35.2 |
| | 25 | 53.7 | 34.9 |
| Barbituric Acid | 0 | 45.9 | 36.0 |
| | 5 | 62.5 | 39.5 |
| | 10 | 72.8 | 42.1 |
| | 15 | 73.1 | 42.2 |
| | 20 | 70.7 | 41.4 |
| | 25 | 67.2 | 40.2 |
| Uric Acid | 0 | 10.0 | 9.8 |
| | 10 | 16.2 | 16.4 |
| | 15 | 20.1 | 18.8 |
| | 20 | 19.8 | 19.3 |
| | 25 | 19.6 | 19.2 |
| | 30 | 19.6 | 19.3 |
| | 35 | 19.8 | 19.3 |
| Adenine | 0 | 63.6 | 48.5 |
| | 10 | 56.8 | 44.7 |
| | 15 | 59.6 | 38.6 |
| | 20 | 58.0 | 36.7 |
| | 25 | 53.8 | 35.0 |
| | 30 | 56.0 | 35.9 |
| | 35 | 63.3 | 38.8 |
| | 40 | 57.8 | 36.6 |
| Carbazole | 0 | 49.0 | 40.2 |
| | 10 | 39.6 | 35.1 |
| Cytozine | 0 | 29.4 | 25.8 |
| | 10 | 36.6 | 27.3 |
| | 15 | 43.2 | 32.3 |
| | 20 | 47.6 | 33.9 |
| | 25 | 49.4 | 33.1 |
| | 30 | 43.5 | 30.3 |
| | 35 | 49.7 | 33.2 |
| Thymine | 0 | 53.9 | 39.5 |
| | 10 | 67.7 | 44.5 |
| | 15 | 77.0 | 44.4 |
| | 20 | 82.1 | 45.3 |
| | 25 | 78.3 | 43.9 |
| | 30 | 72.3 | 42.0 |
| | 35 | 75.3 | 43.0 |
| | 40 | 68.4 | 40.6 |
| Uracil | 0 | 17.6 | 17.2 |
| | 10 | 28.8 | 25.5 |
| | 15 | 39.6 | 31.1 |
| | 20 | 47.5 | 36.6 |
| | 25 | 51.1 | 38.0 |
| | 30 | 56.1 | 39.4 |
| | 35 | 50.0 | 33.3 |
| | 40 | 46.6 | 31.8 |

[a] HC in the product of reaction of 1 mol of cyclohexanone with 5 mol of formadehyde (5-HMCH).
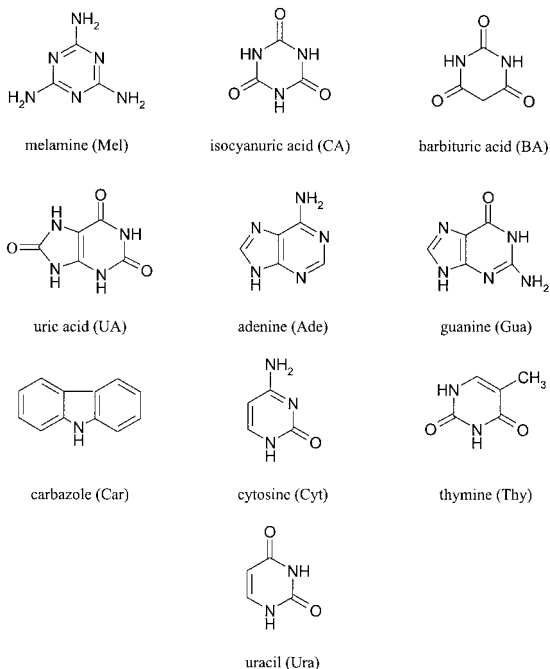[b] $R_{HC}$ g/100 g per final amount of RS.

**Table III   Curing of Melamine Solutions**[a]

| Catalyst | | Water Added (g/100 g RS) | Amount of Melamine Added (g/100 g RS) | Remarks |
|---|---|---|---|---|
| Kind | Amount (wt %) | | | |
| – | – | 25 | 60 | Opaque, heavily blistered |
| | | 30 | 66.6 | |
| | | 30 | 76.8 | |
| 80% HCOOH | 0.5 | 25 | 69.9 | Opaque, rough surface |
| | | 30 | 99.9 | Transparent, brittle |
| | 1 | 25 | 60.0 | Transparent, brittle |
| | | | 69.9 | |
| | | 30 | 89.8 | Transparent, brittle |
| | | | 99.8 | |
| | | | 100.0 | |
| | | | 106.6 | Hard, opaque, rough surface |
| | 2 | 30 | 99.7 | Hard, opaque, rough surface |
| 36% HCl | 0.5 | 20 | 49.9 | Hard, transparent, smooth surface |
| | | | 59.9 | Brittle, transparent |
| | | 25 | 69.9 | Hard, pearly |
| | | 30 | 99.8 | Hard, pearly |
| | 1 | 20 | 49.9 | Brittle, pearly |
| | | | 60.0 | |
| | | 25 | 69.9 | Pretty hard, transparent, slightly blistered |
| | | | 83.3 | Hard, rough surface |
| | | 30 | 89.9 | Hard, pearly |
| | | | 99.9 | Hard, pearly, slightly blistered |
| | | | 106.6 | Hard, smooth, opaque |
| | | 35 | 116.6 | Hard, smooth, white |
| | 2 | 20 | 49.9 | Brittle, transparent |
| | | | 59.9 | |
| | | 25 | 69.9 | Hard, white |
| | | | 83.3 | |
| | | | 90.0 | |
| | | 30 | 99.9 | Hard, white |
| | | 35 | 116.6 | |
| 80% CH$_3$COOH | 2 | 25 | 69.9 | Brittle, pearly |
| | | | 106.4 | |

a

conversion at which no change in the concentration was observed was taken as the equilibrium conversion (Fig. 1). The molar ratio of cyclohexanone to formaldehyde in the dehydrated product was determined from mass balance. The product was isolated by distilling off water under reduced pressure. The distillation was carried out carefully so that the temperature did not exceed 50°C. A slow dehydration of the resulting aldol was observed, which, in turn, reduced the solubilization power of the reactive solvent. The yield of anhydrous reactive solvent was close to 100% relative to the cyclohexanone introduced. The RS,



**Figure 1**   The content of CH$_2$O during the reaction of 1 mol of cyclohexanone with 5 mol of formaldehyde.

the product of reaction of 1 mol of cyclohexanone with 5 mol of formaldehyde (5-HMCH) obtained from a mixture of cyclohexanone to formaldehyde with the molar ratio 1:5, was a thick clear and colorless liquid containing 22.3 wt % of free formaldehyde, a refractive index of $n_{20}^{D} = 1.4801$, density $\rho_{20}^{4} = 1.28$ gcm$^{-3}$, viscosity, $\eta = 1.9$ Pa · s. 5-HMCH was found to have the best solvating power with respect to melamine.

Its approximate structure can be written as:

$$
\begin{array}{c}
\text{H}-(\text{OH}_2\text{C})_z \\
\text{H}-(\text{OH}_2\text{C})_w
\end{array}
\underset{\text{(cyclohexane ring with O at top)}}{\bigcirc}
\begin{array}{c}
(\text{CH}_2\text{O})_x-\text{H} \\
(\text{CH}_2\text{O})_y-\text{H}
\end{array}
\qquad (7)
$$

$$(w+x+y+z=5).$$

The structure of this compound was confirmed by $^1$H NMR and IR analysis. In $^1$H-NMR spectrum of 5-HMCH the signals are observed at:[2,11]

- 2.1–2.4 ppm from $\alpha$-methylene groups (relative to carbonyl group)

- 1.5–1.9 ppm from protons $C_3$ and $C_4$ of cyklohexanone ring
- 3.1–3.9 ppm from methylene groups in -C$\underline{H}_2$-OH
- 5.5–6.4 ppm from —OH group (broad signal due to intermolecular hydrogen bonding).

The intensity of the last signal decreased as heavy water was added thus demonstrating the correctness of its assignment.

In the spectrum of 5-HMCH the signals were also found from methylene protons in the groups obtained by the subsequent addition of formaldehyde to an existing hydroxymethyl group (at 4.65–4.8 ppm). The presence of this grouping was found to favor melamine solubilization. Furthermore, a signal at 4.45–4.65 ppm from protons in polyoxymethylene bridges: —CH$_2$—O—CH$_2$—O—CH$_2$— was present in the spectrum confirming that condensation of hemiacetal groups did occur during RS synthesis.

$$
\begin{array}{c}
\text{O} \\
| \quad || \quad | \\
-\text{C}-\text{C}-\text{C}-\text{CH}_2\text{O}-\text{CH}_2\text{OH} + \text{HOCH}_2-\text{C}-\text{C}-\text{C}- \rightleftarrows \\
| \qquad | \qquad\qquad\qquad\qquad\qquad | \quad | \\
\end{array}
$$

$$
\begin{array}{c}
\text{O} \qquad\qquad\qquad\qquad\qquad\qquad \text{O} \\
| \quad || \quad | \qquad\qquad\qquad\qquad | \quad || \quad | \\
-\text{C}-\text{C}-\text{C}-\text{CH}_2\text{O}-\text{CH}_2\text{O}-\text{CH}_2-\text{C}-\text{C}-\text{C}- + \text{H}_2\text{O} \qquad (8) \\
| \qquad | \qquad\qquad\qquad\qquad\qquad | \quad |
\end{array}
$$

The proportions of groupings —O—CH$_2$—OH, —CH$_2$—O—CH$_2$—O—CH$_2$— and —C—CH$_2$—O— calculated from the spectrum were 0.78, 1.33 and 3.2 moles per mole of RS, respectively.

IR spectra of 5-HMCH contain:[12]

- strong stretching vibrations at 3382 cm$^{-1}$ from —OH groups (poly associates),
- at 1309–1277 cm$^{-1}$ and 1017–931 cm$^{-1}$ deformational vibrations from —OH groups and stretching from C-O (conjugated, typical for primary alcohols), respectively,
- strong stretching vibrations at 2933 cm$^{-1}$ and at 2859 cm$^{-1}$ from methylene groups in the ring (asymmetrical and symmetrical, respectively),
- at 1703 cm$^{-1}$ stretching from carbonyl group,

- in the range 1410–1450 cm$^{-1}$ from deformational vibrations of the ring methylene groups, and from skeleton vibrations at
- 750 cm$^{-1}$,
- at 2795 cm$^{-1}$ (stretching from —C—H$_{—O—CH2—O—}$) and at 1109 cm$^{-1}$ (asymmetrical of
- —C—O—C—) which confirm observations in $^1$H NMR spectra on the presence of condensation products and addition of subsequent formaldehyde molecule to existing hydroxymethyl groups.

As mentioned above, the RS (5-HMCH) was tested to dissolve heterocyclic compounds other than melamine. The following compounds containing NH groups were selected:

melamine (Mel)          isocyanuric acid (CA)          barbituric acid (BA)

uric acid (UA)          adenine (Ade)          guanine (Gua)

carbazole (Car)          cytosine (Cyt)          thymine (Thy)

uracil (Ura)

The amount of compound dissolved has been found to depend on its structure, the method of introduction and the amount of water present in RS.

By the single introduction method (see Experimental section), 26.4 g of melamine dissolved in 100 g of RS. After introducing water, the amount increased substantially up to 103.2 g per 100 g of RS (Table II). Isocyanuric and barbituric acids dissolved up to 56.7 and 83.3 g per 100 g of RS, respectively, at the presence of 25 wt % of water (Table II). The solubility did not practically change at water content in RS exceeding ca. 15 wt %. The solubility of uric acid was relatively small and did not exceed 20.2 g/100 g RS. While adding adenine in one portion, the solubility was 63.7 g, the maximum at 30 wt % content of water was 75.7 g/ 100g of RS. More water reduced adenine solubility. Guanine was found insoluble both in pure RS or in RS diluted with water.

Carbazole introduced in one portion dissolved in the amount of 49.1g/100 g of RS. Addition of 10% of water reduced the solubility to 37.3 g/100 g of RS (Table II). The reason might be the total lack of solubility of this compound in water. The time needed to dissolve carbazole was particularly long (25–70 min), as compared with solubilization time for other compounds (10 min). The color of carbazole solution was brown. A solid precipitated from the solution when it was cooled.

30.0 g of cytosine added in one portion was dissolved in 100 g of RS. Introduction of water improved the solubility of the compound up to 53 g/100 g of RS at 35 wt % of water (Table II).

Thymine and uracil added in one portion dissolved in the amount of 53.5 g and 18 g per 100 g of RS, respectively. At above 20% of water in RS, solubility of the compounds increased only slightly. The highest solubility of thymine and uracil was 84.8 and 57.6g/100 g RS, respectively.

The nature of solubility of melamine and other heterocyclic compounds in reactive solvents consists of a reaction of the compounds with solvent molecules. In case of 5-HMCH solvent, the reaction is the formation of N-hydroxymethyl derivatives of the compounds (compare with the reactions of 4 and 5). Hydroxymethyl derivatives may be expected to form from formaldehyde released by RS (compare reactions 2–4). Water is formed in the reaction and the compound is being built into the solvent structure by condensation of its hydroxymethyl groups with those of RS (reaction 5).

Water evaporates while the sample is heated. Extra portions of water added to RS improve the solubility of nitrogen containing heterocyclic compounds (except of guanine and carbazole, where it is neutral or reduces solubility, respectively). Water acts therefore in two ways. It physically dissolves some part of the compound and facilitates breaking up of hemiacetal groups and formaldehyde release. The compounds dissolve in RS provided they have hydrogen atoms at nitrogen that can react with formaldehyde. An absence of these protons reduces dissolution of a compound to the physical one. This has been verified for several compounds, including picolinic, nicotinic, and isonicotinic acids, which precipitated from the solution upon cooling.

The basis for dissolution of a heterocyclic compound in RS is the presence of an active proton at nitrogen in the heterocycle that can react with formaldehyde. The solubility is not the largest when it is gradually introduced into the solution. The reason might be cyclization and linear condensation involving molecules of RS itself (reaction 8).[2] Then its solvating power towards, for example, melamine, would decrease.
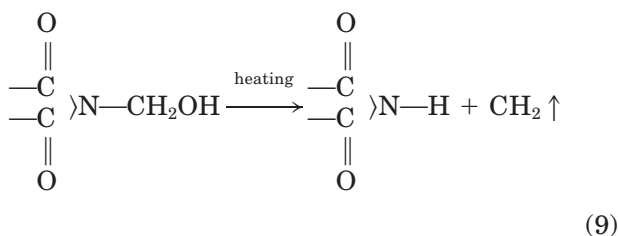
By introducing a compound in one step (in the amount determined by the gradual introduction step method) several additional percentage of the compound can be dissolved. After introducing 10% of water to RS the solubility increased by another several percent. Each increase in water content in RS, by 5% portions, up to 40 wt % led to a further increase of solubility.

The changes in solubility of heterocyclic compounds in RS clearly indicates that the dissolution is accompanied by chemical reaction (reactions 2–4). The hydroxymethyl derivatives of the compounds react with similar groups in the solvent to increase the solubility (reaction 4).

The solubility of heterocyclic compounds in reactive solvents increases with increasing temperature (80–120°C). Above 100°C water formed in condensation reactions evaporates along with water introduced to the system and other volatile compounds. At 120°C the solutions are practically anhydrous liquids.[3]

Preliminary experiments were performed on curing the solutions of heterocyclic compounds in RS with concentrated acids (hydrochloric, acetic, and formic) (Table III). To the solution of a heterocyclic compound, 0.5– 2 wt % of acid was added with respect to the mass of RS. The sampled were poured on degreased glass plates and kept at 120°C. Different amounts of heterocyclic compounds were used in the curing experiments. The experiments were made with solutions of melamine, barbituric acid, adenine, cytosine, uracyl, or carbazole. A positive result was obtained for the melamine solution. The samples obtained from adenine barely cured, became yellow and slightly blistered. The sample from barbituric acid was heavily blistered.

The coatings obtained from cytosine become yellow during the curing and were blistered, as well. Attempts of curing carbazole, uracyl, or isocyanuric acid solutions failed altogether, since either the solution did not harden or the compound precipitated from the solution (uracyl or isocyanuric acid). The reason might be the instability of *N*-hydroxymethyl groupings in the compounds and recovery of amide groups at elevated temperatures. Such an instability has been observed for isocyanuric acid before.[13]

$$\text{—C}\langle \begin{matrix} O \\ \| \\ \text{C} \\ \text{C} \\ \| \\ O \end{matrix} \rangle\text{N—CH}_2\text{OH} \xrightarrow{\text{heating}} \begin{matrix} O \\ \| \\ \text{C} \\ \text{C} \\ \| \\ O \end{matrix}\rangle\text{N—H} + \text{CH}_2 \uparrow$$

(9)

The coatings obtained by curing barbituric acid solutions were heavily blistered (Zarzyka I, private communication). The compound has four functionalities reacting with formaldehyde: two imide groups and the bifunctional methylene group, which takes part in aldol condensation reactions. Like in isocyanuric acid, however, *N*-hydroxymethyl groupings are instable and cannot take a significant part in curing processes. Probably, the cross-linking take place via C-hydroxymethyl groups formed in reactions of methylene groups with formaldehyde.

$$\text{—C—CH}_2\text{—OH} + \text{HO—CH}_2\text{—C—} \rightarrow$$

$$\rightarrow \text{—C—CH}_2\text{—O—CH}_2\text{—C—} + \text{H}_2\text{O}$$

(10)
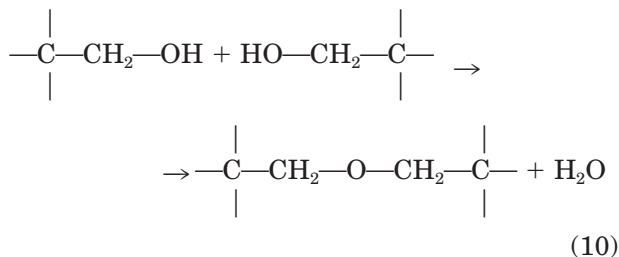
In the curing process, the solutions quickly become very viscous, and formaldehyde released from the system is responsible for blistering.

The best quality coatings were obtained from melamine solutions. They were well hardened, transparent and usually free of blisters.

## CONCLUSIONS

Certain nitrogen containing heterocyclic compounds, such as adenine, carbazole, cytozine, guanine, thymine, and uracyl, as well as isocyanuric, barbituric, and uric acids, dissolve in the reactive solvent obtained by reacting 1 mol of cyclohexanone with 5 mol of formaldehyde. The dissolution consists of the reaction of formaldehyde released from reactive solvent with amino groups of heterocyclic compounds and the subsequent condensation of the resulting hydroxymethyl groups with those of reactive solvent. Products of dissolution of melamine in the reactive solvent 5-HMCH yield solutions that can be used as substrates in preparation of new group of polycondensation materials. The solutions can be cured with acidic catalysts at 120° C to obtain materials of promising properties.

Details on the properties of melamine-cyclohexanone-formaldehyde resins will be published in a forthcoming article.

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