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CO-CONDENSATION OF (ALKYL)RESORCINOLS WITH METHYLOLUREAS

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The co-condensation between resorcinols, including the most typical components of oil shale alkylresorcinols (5-methylresorcinol, 2,5-dimethylresorcinol), and methylol-N,N-diethylurea or monomethylolurea is the favoured reaction in the presence of acid catalyst. Methylene ^1H chemical shifts are assigned and the integrals of signals used for determination of co-condensate methylene molar concentration. C4 monosubstituted and C4C6 disubstituted resorcinols are the predominant structural elements of co-condensates.

Introduction

Resorcinol-formaldehyde (RF) resins have a high rate of curing without acidic catalysts and give glued materials with excellent resistance to hydrolysis. The high cost of resorcinol has promoted the application of co-condensation resins with a smaller content of resorcinol. The use of phenol-resorcinol-formaldehyde co-condensate prepolymers for production of laminated timber represents the best example. The co-condensate resin of the same quality has been obtained, substituting the resorcinol by oil shale alkylresorcinols containing about 50 % of 5-methylresorcinol [1]. The other preferred components of alkylresorcinols mixture are 5-ethylresorcinol, 2,5- and 4,5-dimethylresorcinols. The initial binding of formaldehyde to phenol of lesser reactivity favours the co-condensation with resorcinols in all catalytic conditions [2]. The stability of methylol-phenols and the high tendency of resorcinols to polycondensation are the two most important specifics leading to quantitative co-condensation.

Another situation occurs in urea-resorcinol-formaldehyde condensation. There are no problems in synthesizing two methylol derivatives of urea in special conditions. The equilibrium of methylol formation in the presence

of alkaline catalyst promotes the dissociation of methylol derivatives and the polycondensation of released formaldehyde with resorcinol. The higher affinity of 5-methylresorcinol to formaldehyde makes for the last reaction. Unlike RF reaction, only the acidic catalyst leads to successful polycondensation of methylolureas. In our case the formaldehyde is linked to co-reagent of higher reactivity and the key question is the relative affinity of resorcinol and urea to polycondensation with methylolureas. The well-known preferential polycondensation in RF reaction presumes the successful co-condensation as well.

The equilibrium of urea-formaldehyde (UF) reaction and the low C-N (or C-O) bond energy are the main reasons inducing free formaldehyde and hydrolytic resistance problems of UF-bonded materials. Alongside of using UF resins of low mole type with higher dosage of resin and hydrofobing agent the using modified (fortified) UF resins is the problem of great topicality [3]. Among the used modifiers resorcinol seems to be the most effective formaldehyde scavenger and fortifier for increasing the hydrolysis resistance [4, 5]. The decrease of free formaldehyde content and the improvement of physico-mechanical properties of particleboards are also obtained in using UF resins modified by oil shale alkylresorcinols [6, 7]. Resorcinol terminated UF resin was synthesized by co-condensation of methylol containing UF prepolymers with resorcinol in the presence of acid catalyst (*para*-toluenesulfonic acid). That resin is resistant to heat hydrolysis and is useful for exterior use in plywood and laminated timber [8]. ^1H NMR study of reaction product of dimethylolurea and 5-methylresorcinol (1/2) has shown that 64 % of methylene groups are involved to co-condensates [9]. Pure methylene compounds of mono- or disubstituted urea and C4 substituted resorcinol were isolated from the reaction mixture of mono- or dimethylolurea with the excess of resorcinol [10].

In this work, the co-condensation of resorcinols with methylolureas was studied on model compounds. Resorcinol, as the main highly reactive phenol of commercial interest, was included. 5-Methylresorcinol was specifically chosen as the most reactive resorcinol and the most abundant component in oil shale alkylresorcinols. 2,5-Dimethylresorcinol is the other typical and available component of the latter raw. We expect that methylol-*N,N*-diethylurea quite well models the methylolurea type reagent, but due to monofunctionality gives products of better solubility and the interpretation is more successful. Monomethylolurea, as the first-formed compound of urea-formaldehyde reaction, was the other methylol compound used. Evidently, the free reactive amino group of the last compound creates more complicated situation for co-condensation. The main purpose of this study was to ascertain the conditions for obtaining the maximum amount of co-condensate. ^1H NMR study was used for identification and determination of methylene group distribution between structural elements.

Experimental

Materials

Commercial grade resorcinol (R) and 5-methylresorcinol (5MR) were recrystallized from benzene (m.p. 110.8 °C and 110.2 °C, respectively). 2,5-Dimethylresorcinol (2,5DMR) was separated from oil shale alkyl-resorcinols at the Institute of Chemistry (m.p. 161.5 °C, content of main substance 98.4 %). The fraction of oil shale alkylresorcinols "Alkyres" with the content of 51.5 % of 5MR and separated by rectification from its concentrate of 5MR (71.6 %) were also used in some experiments. Monomethylolurea (MMU) was prepared from urea and 37 % aqueous solution of formaldehyde (2/1) in the presence of Na₂HPO₄ at 25 °C (2 h) and 0 °C (24 h). Solidified MMU was recrystallized twice from ethanol (m.p. 111 °C). Methylol-*N,N*-diethylurea (MDEU) was synthesized from *N,N*-diethylurea and formaldehyde with equimolar ratio of reagents analogically, and after solidification recrystallized from diethyl ether (m.p. 98 °C).

Studied Systems

Co-condensation reactions of methylolureas with resorcinols were performed in the melt at 100 °C (1 h) and in the aqueous solution at 30 °C (or 40 °C) depending on reaction rate during 1-4 days or 1 h in the presence of the *para*-toluenesulfonic acid (*p*-TSA) catalyst. The following molar ratios were used:

$$\begin{aligned} \text{MDEU or MMU / R or 5MR or 2,5DMR / } p\text{-TSA} &= \\ &= 1 / 1 / 0.01(0.001) \text{ or } 2 / 1 / 0.01 \end{aligned}$$

$$\begin{aligned} \text{MDEU or MMU / R or 5MR or 2,5DMR / } p\text{-TSA / water} &= \\ &= 1 / 1 / 0.01(0.1) / 20\text{-}40 \text{ or } 2 / 1 / 0.01(0.1) / 20\text{-}40 \end{aligned}$$

$$\begin{aligned} \text{MMU / Alkyres or 5MR concentrate / } p\text{-TSA / water} &= \\ &= 2 / 1 / 0.1 / 20 \end{aligned}$$

Some experiments were performed in the same conditions without catalyst.

For comparison the self-condensates of MDEU and MMU were prepared in melt condensation at 100 °C (12 h and 1 h).

¹H NMR Measurement

Methylene ¹H chemical shifts were found in 100 MHz spectra for methylene compounds (products) and for methylol and dimethylene ether derivatives of ureas. Deuterated dimethylsulfoxide (DMSO) and pyridine (Py) were used as NMR solvents. Methylene ¹H shifts were measured from internal hexamethyldisiloxane in Py and from sodium salt of 2,2-dimethyl-2-silapentane-5-sulfonic acid (DSS) in DMSO and

referenced to tetramethylsilane (TMS). Quantitative molar methylene concentrations were calculated from integral intensities of the corresponding methylene ^1H signals. In case of aqueous solutions the two phase reaction products were separated and analyzed after drying in vacuum. The methylene concentrations were calculated considering the shares of both phases.

Results and Discussion

Generally, the reaction products contain methylenes in three different environment: $-\text{NH}-\text{CH}_2-\text{Ar}-$ in co-condensates, $-\text{NH}-\text{CH}_2-\text{NH}-$ in methylolurea self-condensates, and $-\text{Ar}-\text{CH}_2-\text{Ar}-$ in RF homocondensates. This specific feature is the main point for a successful ^1H chemical shifts assignment. Evidently, the substantial shifts of methylene ^1H signals occur with complicated polycondensates due to the presence of methylenes in different environment in the same molecule. Only in case of methylolurea self-condensates dimethylene ethers as intermediates are present. The condensation products in case of participation of resorcinols contain only methylene groups.

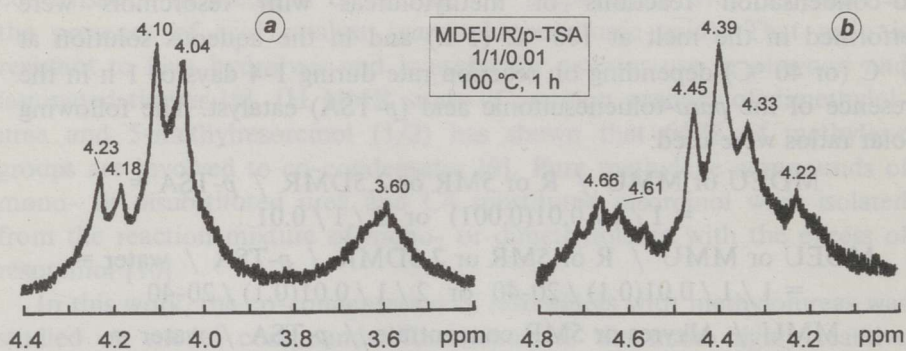


Fig. 1. ^1H NMR spectrum of methylol-*N,N*-diethylurea and resorcinol reaction product: a - in $\text{DMSO}-d_6$; b - in $\text{pyridine}-d_5$

Table 1. Methylene ^1H Chemical Shifts of Methylolurea Self-Condensates

Compound	Solvent	Methylol	Dimethylene ether	Methylene
Methylol- <i>N,N</i> -diethylurea	$(\text{CD}_3)_2\text{SO}$	4.55	4.62	4.45
	$\text{C}_5\text{D}_5\text{N}$	5.11	5.02	4.87
Monomethylol urea	$(\text{CD}_3)_2\text{SO}$	4.49	4.56	4.28
				(4.30-4.35)
	$\text{C}_5\text{D}_5\text{N}$	5.10	5.01	4.72
				(4.75-4.85)

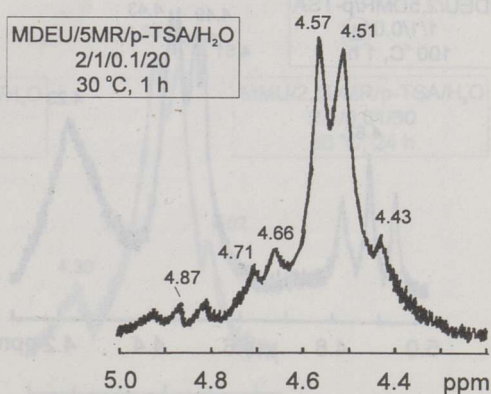
^1H NMR Assignment

The registration ^1H NMR spectra in two different solvents is essential considering the location of ^1H shifts and solubility of products. The main preference of DMSO in comparison with Py lies in the well-resolved upfield ^1H signal of $-\text{Ar}-\text{CH}_2-\text{Ar}-$ (e.g. Fig. 1). The spectra in Py are more effective for calculating of the content of $-\text{NH}-\text{CH}_2-\text{NH}-$ (Table 1) and C2 substitution in co-condensates (Table 2). The products with MDEU are soluble in both Py and DMSO. In case of MMU the products are fully soluble in DMSO and partly in Py, mainly due to the bad solubility of MMU-self-condensate and also of C4C6 substituted co-condensates in case of 2/1 ratios of co-reagents. Methylene ^1H shifts of MMU-self-condensates in Py are obtained on the basis of mixtures due to the co-solubility (Table 1).

Table 2. Methylene ^1H Chemical Shifts of Co-Condensates

Resorcinolic compound	$\text{C}_5\text{D}_5\text{N}$			$(\text{CD}_3)_2\text{SO}$		
	C4	C4C6	C2	C4	C4C6	C2
Methylol-<i>N,N</i>-diethylurea						
Resorcinol	4.43	4.36	4.55-4.70	4.07	4.07	4.2-4.3
5-Methylresorcinol	4.53	4.53	4.60-4.70	4.07	4.13	4.2-4.3
2,5-Dimethylresorcinol	4.48	4.46	-	4.09	4.14	-
Monomethylolurea						
Resorcinol	4.52	4.45	4.65-4.75	4.06	4.06	4.2-4.3
5-Methylresorcinol	4.50	4.46	4.60-4.70	4.06	4.12	4.2-4.3
2,5-Dimethylresorcinol	4.44	4.44	-	4.05	4.10	-

Fig. 2. ^1H NMR spectrum of methylol-*N,N*-diethylurea and 5-methylresorcinol reaction product in pyridine- d_5



One can see from Table 2 that in both solvents the ^1H signals of co-condensate methylenes appear in a quite narrow region, depending not very much on used reagents. The influence of strongly electronegative

nitrogen determines the location of well-resolved ^1H signal of co-condensate methylene between methylene ^1H signals of homo-condensates of both types. The downfield shift of signals in Py is predicted because of strong mutual orientation between phenolic hydroxyl and Py nitrogen. The effect of two *ortho*-hydroxyls is responsible for the greatest downfield shift of C2 substituted methylene signals but in DMSO the mentioned signal appears only as a shoulder. The methylenes give doublet ^1H signals due to interaction with amine hydrogen. The resolution is not always sufficient in DMSO solution to registrate two peaks, especially in the presence of C4 and C4C6 substituted methylenes in comparable amounts.

The substitution in resorcinols occurs mainly in two equal positions. The methylene ^1H shift from disubstitution in comparison with monosubstitution depends on used NMR solvent (Table 2). It appears in the lower field in DMSO and in the upper field in Py. The difference between the mentioned shifts is greatest in the system MDEU/R in Py (Fig. 1). One resolved signal of both doublets allows to estimate the ratio of C4 and C4C6 substituted compounds. Generally, the difference between signals from C4 and C4C6 substitution is not great and in many cases the signals coincide (e.g. Fig. 2). C2 methylenes give more than one signal in the region of 4.55–4.75 ppm, belonging probably to mono-, di- or trisubstituted resorcinols. It is not possible to determine the content of 5MRF resin from spectra in Py (4.43 ppm). The spectra in DMSO has the well-resolved signal for 5MRF resin (3.75–3.80 ppm). The substitution in 2,5DMR occurs only in two positions. Due to small difference of corresponding signals (Fig. 3), the ratio of C4 and C4C6 substituted compounds can not be estimated.

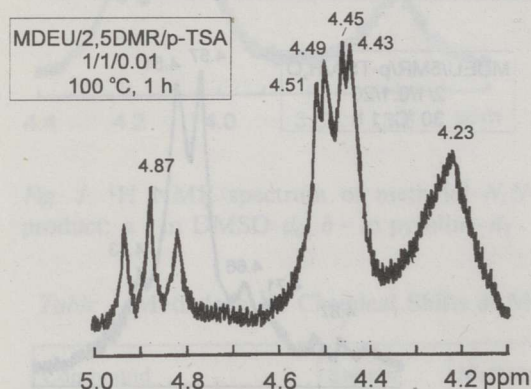


Fig. 3. ^1H NMR spectrum of methylol-*N,N*-diethylurea and 2,5-dimethylresorcinol reaction product in pyridine- d_5

The appearance of methylene ^1H shifts of MMU self-condensates in comparison with methylene-*N,N*-diethylurea in the upper field (Table 1) and the polymeric character of self-condensate do not favour the interpretation of spectra. It is also possible that the MMU self-condensates are the constituents of co-condensates causing the shift of corresponding

Fig. 4. ^1H NMR spectrum of monomethylolurea and 5-methylresorcinol reaction product in pyridine- d_5

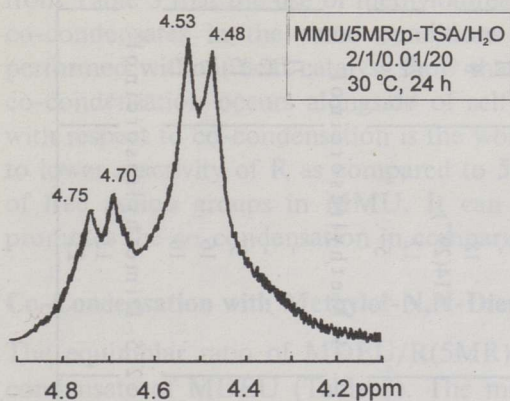
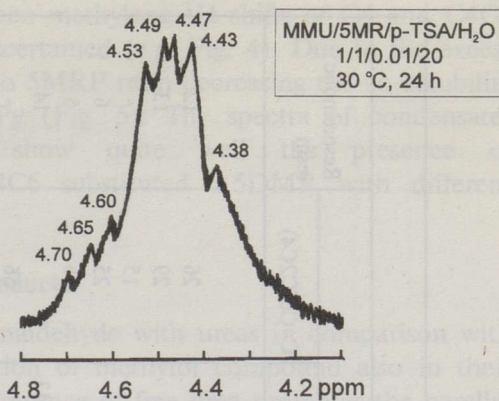


Fig. 5. ^1H NMR spectrum of monomethylolurea and 5-methylresorcinol reaction product in pyridine- d_5

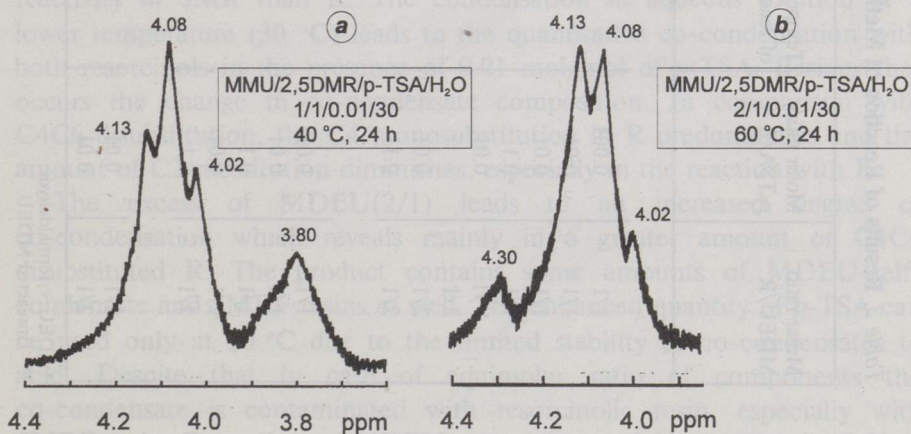


Fig. 6. ^1H NMR spectrum of monomethylolurea and 2,5-dimethylresorcinol reaction product in $\text{DMSO}-d_6$

Table 3. Results of Reaction of Methylol-*N,N*-diethylurea with Resorcinols

Molar ratio MDEU/R	Molar ratio <i>p</i> -TSA/R	Temperature of reaction, °C	Distribution of methylene, molar %					Resorcinolic resin
			Methylenedi- <i>N,N</i> -diethylurea		Co-condensate			
					C2	C4	C4C6(C2C4)	
Resorcinol								
1/1	0.001	100	-	22	40	26	12	
1/1	0.01	100	-	24	34	29	13	
1/1	0.01	30	-	10	75	15	-	
1/1	0.1	30	-	11	58	25	6	
1*/1	0.01	30	18	8	53	16	5	
2/1	-	30	14(29**)		43		14	
2/1	0.01	100	12	20	12	56	-	
2/1	0.1	30	5	8	18	64	5	
5-Methylresorcinol								
1/1	0.01	100	-	21		53	26	
1/1	0.01	30	-	15		85	-	
1/1	0.1	30	5	15		56	24	
2/1	0.01	100	16	17		56	11	
2/1	0.1	30	10	13		67	10	
2,5-Dimethylresorcinol								
1/1	0.01	100	13	-		54	33	
2/1	0.01	100	21	-		64	15	

* DEU + formaldehyde.

** Unreacted MDEU.

^1H signals. The difference between methylene ^1H shifts of C4 and C4C6 substituted R or 5MR can be ascertained (e.g. Fig. 4). Due to the excess of MMU the product contains no 5MRF resin decreasing the co-solubility of C4C6 substituted 5MR in Py (Fig. 5). The spectra of condensates MMU/2,5DMR in DMSO show quite well the presence of co-condensates of C4 and C4C6 substituted 2,5DMR with different methylene shifts (Fig. 6).

Composition of Condensation Products

The preferential reaction of formaldehyde with ureas in comparison with resorcinols presumes the formation of methylol compound also in their mixture. At the same time the presence of free urea promotes the parallel reaction of the last with the formed methylol compound. One can see from Table 3 that the use of methylolureas is suitable as higher amounts of co-condensates in the same conditions are formed. Some experiments performed without acid catalyst show that the reaction rate is low and the co-condensation occurs alongside of self-condensation. At this the result with respect to co-condensation is the worst in the system of MMU/R due to lower reactivity of R as compared to 5MR and because of the presence of free amino groups in MMU. It can be concluded that acid catalyst promotes the co-condensation in comparison with other reactions.

Co-Condensation with Methylol-N,N-Diethylurea

The equimolar ratio of MDEU/R(5MR) excludes the formation of self-condensate of MDEU (Table 3). The melt-condensation at 100 °C gives mainly the co-condensate but the product contains also some amount of RF-resin. The content of 5MRF-resin is greater due to the higher reactivity of 5MR than R. The condensation in aqueous solution at a lower temperature (30 °C) leads to the quantitative co-condensation with both resorcinols in the presence of 0.01 mol/mol of *p*-TSA. Besides that occurs the change in co-condensate composition. In comparison with C4C6 disubstitution, the C4 monosubstitution in R predominates and the amount of C2 substitution diminishes, especially in the reaction with R.

The excess of MDEU(2/1) leads to an increased degree of co-condensation which reveals mainly in a greater amount of C4C6 disubstituted R. The product contains some amounts of MDEU-self-condensate and 5MRF resins as well. The enhanced quantity of *p*-TSA can be used only at 30 °C due to the limited stability of co-condensates to acid. Despite that in case of equimolar ratio of components the co-condensate is contaminated with resorcinolic resin, especially with 5MRF resin. Regardless of MDEU excess the product contains 5-10 % of RF (or 5MRF) resin as the energetically most preferred methylene compound.

Table 4. Results of Reaction of Monomethylolurea with Resorcinols

Molar ratio MMU/R	Molar ratio <i>p</i> -TSA/R	Temperature of reaction, °C	Distribution of methylene, molar %					Resorcinolic resin
			Methyleneureas		Co-condensate			
			C2	C4	C2	C4	C4C6(C2C4)	
Resorcinol								
1/1	0.01	100	-	-	55	-	45	
1/1	0.01	30	-	10	-	68	22	
1/2	0.005	100	-	16	-	-	54	
2/1	0.01	100	26	-	23	7	24	
2/1	0.01	30	25	-	50	-	5	
2/1	-	40	44(21*)	-	70	-	3	
2/1	0.1	30	18	-	32	-	7	
5-Methylresorcinol								
1/1	0.01	100	12	17	-	-	32	
1/1	0.01	30	-	13	-	39	33	
2/1	0.01	100	42	-	43	54	15	
2/1	0.01	30	23	-	77	-	-	
2/1	-	40	34	-	57	-	9	
2,5-Dimethylresorcinol								
1/1	0.1	100	18	-	-	41	41	
1/1	0.1	40	-	-	-	75	25	
2/1	0.1	100	40	-	-	40	20	
2/1	0.1	40	35	-	-	60	5	
2/1	0.1	60	10	-	-	90	-	

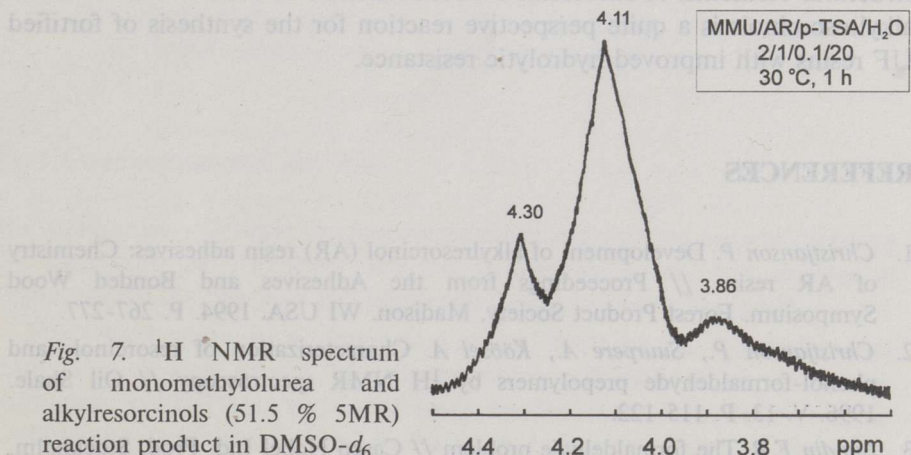
* Unreacted MMU.

The low reaction rate with 0.01 mole of *p*-TSA at 30 °C can be overcome by increasing the reaction temperature of aqueous solution.

Tendency of 2,5DMR to co-condensation is lowest among the studied resorcinols. Depending on molar ratio of components the condensation product contains self-condensate of MDEU and 2,5 DMRF resin in different ratio.

Co-Condensation with Monomethylolurea

The equilibrium of UF reaction is the main reason leading to greater content of resorcinolic resin in condensation of equimolar mixture of MMU with resorcinols (Table 4). Unlike MDEU the condensation at lower temperature (30-40 °C) in aqueous solution does not give the quantitative co-condensation. The co-condensation can be regarded as the predominant reaction (67-78 %). In case of reaction with excess MMU at 30-40 °C the formation of resorcinolic resin can be practically ($\leq 5\%$) avoided. Due to the affinity of amino group to condensation the product contains 25-35 % of UF resin. The higher degree of co-condensation reveals in increased amount of C4C6 disubstituted resorcinols. The isomeric composition of the co-condensate can not be estimated quantitatively because of full solubility of products only in DMSO (Table 4). No significant difference in product composition appears in reaction of MMU/R = 2/1 in the presence of tenfold amount of *p*-TSA in aqueous solution at 30 °C. Low solubility of 2,5DMR in water is responsible for the heterogeneous reaction mixture. At the same time the higher temperature of reaction in water (60 °C) gives the best yield of co-condensate.



The reactions of two examples of oil shale alkylresorcinols (71.6 % and 51.5 % of 5MR, correspondingly) with the excess of MMU (2/1) in the presence of 0.1 mole of *p*-TSA occur preferentially by co-condensation.

The products are fully soluble in DMSO giving the spectra similar to that of MMU/5MR (e.g. Fig. 7). The co-condensate methylenes can be estimated to 70 and 65 % of all methylenes, correspondingly. The high degree of co-condensation shows that other alkylresorcinols participate in the reaction quite successfully, too. A slightly increased amount of alkylresorcinolic resin (~14-17 %) for that ratio of components and a broad methylene signal refer to components in the AR mixture preferring the homo-condensation to co-condensation.

Conclusions

The reaction products of methylol-*N,N*-diethylurea and monomethylolurea with resorcinols, including the most typical components of oil shale alkylresorcinols, contain methylene groups in three different structures: $-\text{NH}-\text{CH}_2-\text{Ar}-$ in co-condensates $-\text{NH}-\text{CH}_2-\text{NH}-$ in methylolurea self-condensates and $-\text{Ar}-\text{CH}_2-\text{Ar}-$ in resorcinol-formaldehyde resins. The ^1H signal of co-condensate methylenes in NMR spectra (4.36-4.53 ppm in Py and 4.05-4.14 ppm in DMSO) was used for the determination of co-condensate amount. The acid catalyst (*p*-TSA) promotes the co-condensation in comparison with other reactions. The co-condensation of resorcinols with MDEU as compared to MMU is favoured. The reaction of equimolar mixture of MDEU/R or 5MR in aqueous solution at 30 °C in the presence of 0.01 mole of *p*-TSA gives the quantitative co-condensation. The co-condensate amount with MMU forms 78 and 67 % in the same conditions. Depending on the molar ratio of components C4 and C4C6 substituted resorcinols are the most preferred structural elements. A successful co-condensation of MMU with oil shale alkylresorcinols is a quite perspective reaction for the synthesis of fortified UF resins with improved hydrolytic resistance.

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Fuel Combustion and Fly Ash

The production of energy by fuel combustion is a process accompanied by the dispersion of chemical elements in the open air, the linking of elements into the biocycle and bioaccumulation in plants and animals.

Fuel combustion in a domestic furnace, boilerhouse, thermal power plant, etc. is one source of environmental pollution. Coal, oil shale, petroleum, natural gas, and wood (to a smaller extent) are used as fuels. Carbon and hydrogen present in fuels are important elements from the point of view of energy. Fuels also contain oxygen, sulfur, nitrogen and numerous macro- and microelements that are in the mineral components [2-5]. These mineral constituents are linked to atmospheric cycles through combustion processes.