FINSKA KEMISTSAMFUNDETS MEDDELANDEN

SUOMEN KEMISTISEURAN TIEDONANTOJA

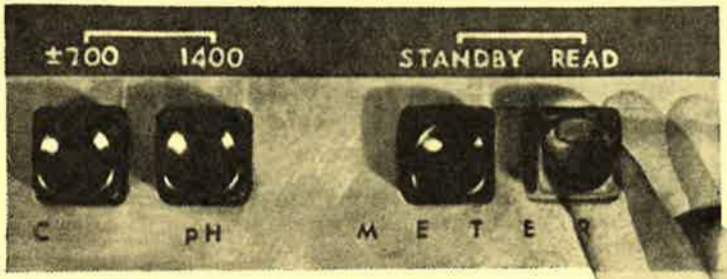
REDAKTÖR — TOIMITTAJA

Tor-Magnus Enari

INNEHÅLL — SISÄLTÖ

N:o 1 · ÅRGÅNG 75 VUOSIK. · 1966

Beckman "Zeromatic II" pH-mätare



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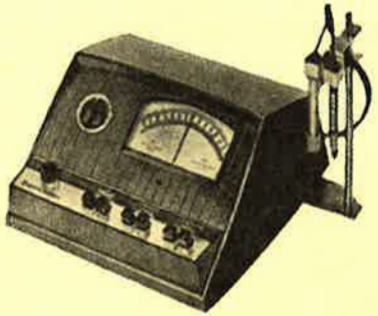

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More Organic Chemicals from the Spent Liquors of the Cellulose Industry*

By *Terje Enkvist* and *Tor Lindfors*

Department of Chemistry of the University of Helsinki—Helsingfors.

Abstract

An outline is given for a process of heating of kraft black liquor with added alkali at common or diminished pressure, giving i.a. the following products: dimethyl sulfide, sodium oxalate, crystallized pyrocatechol and a mixture of its homologues, and homoprotocatechuic acid and its homologues, as well as acetic, formic and succinic acids.

* Mainly corresponding to a lecture in Finnish at the Days for chemistry in Helsingfors on November 24th, 1965. — Patent rights reserved.

Purpose and background of the work.

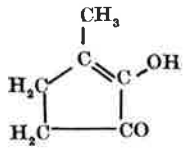
Upon chemical pulping of softwood, usually about half of its weight is dissolved in the spent liquor, pulp for papermaking being the other half. From the spent liquors of kraft cooking, turpentine and tall oil are already isolated as valuable byproducts.

The purpose of the present paper is to report on experiments aiming at manufacture of phenols and various organic acids from spent liquors, especially kraft black liquors, without interfering with the production of cellulose, turpentine or tall oil. These valuable new products will thus come as net addition to the products already produced by the cellulose industry.

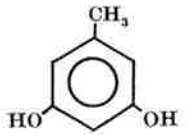
The main method of treatment of the spent liquors has been addition of alkali and heating at temperatures of about 300°C. Several reports concerning this work have been presented [1-7]. Earlier, pressure heating, continuous or periodic, has often been used (cf also [4,8-11]). In the work related in the present report, mainly heatings at common pressure or in vacuum are described. Simplification of the procedures used has been worked out as much as possible.

As basis for the work, a substantial amount of fundamental research has been carried out concerning the properties of lignin, the role of sulfur at kraft cooking and the degradation of lignin and other constituents of wood upon heating with alkaline reagents. The work of *Th. Ashorn* [12], *K. Ekman* [13], *K. Hästbacka* [14] and *C. Juslén-Keller* [15], and recently, *F. Sundholm* [16] belong to this kind of studies. Especially *J. Turunen* [18] has made successful investigations concerning breaking of different bonds of lignin on alkaline heatings, as well as applied research concerning treatment of spent liquors with alkalies. This work has been recently reviewed [18]. The work of Turunen as well as that of other of my coworkers, i.a. *Ruth Stabel-Taucher* [19], (cf also *Lautsch* [10]), show that not only ether bonds, but also bonds between carbon atoms can be broken upon heating with alkaline reagents. Curiously enough, not only lignin, but also sugars such as galactose, glucose, and xylose can give phenols and such enols as 1-methyl-cyclopenten-1-ol-2-one-3 (I) at treatment with alkalies already at 100°C [20].

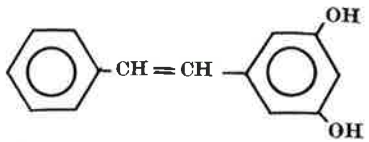
At the study of phenols and acids, chromatography of various kinds has been used extensively by my coworkers and me [21-25]. An important contribution was made by *J. Halmekoski* [26] by use of i.a. chromatography on paper impregnated with sodium tungstate for studies especially of catechol and its derivatives. In addition to gas chromatography [27] thin layer chromatography has been used with success, especially by *G. Nordman*, who further by column and paper chromatography acquired strong indications for the presence of orcinol (II), resorcinol, and pinosylvin (III) in demethylated kraft black liquors.



I. 1-methyl-cyclopenen-1-ol-2-one-3



II. Orcinol



III. Pinosylvin

Performance of heatings with alkali at common or reduced pressure.

At the heatings of spent liquors with alkali at about 300°C, the hydrolysis or demethylation of methoxyl groups in lignin is one of the most important reactions. Such heatings are, therefore, in the following called demethylations. Experiments with various apparatures were made by *E. T. Rinaman*. One of us(L) has carried out a series of demethylations, mostly at reduced pressure (20—130 mm). For this purpose a reactor tube shown in Fig. 1 has been used. This tube is surrounded by an electrically heated oil mantle. The alkali added was dissolved in water, and this alkaline solution was mixed with concentrated kraft black liquor with solids content about 50 %. This reaction mixture was sprayed through a spraying nozzle into the tube, which was already heated to the maximum temperature, for instance 290°C. Usually, the water evaporated during about 1 1/2 hour, the reaction being performed in an almost dry state during about 30 minutes at maximum temperature. After cooling down in an current of nitrogen the reaction product at room temperature was a porous, brittle powder, which filled the reaction tube as a cylindrical lump, leaving a tubular empty space, of only about 1 cm diameter, in the center of the tube. The solid was taken out with aid of an iron rod and stored enclosed in plastic bags to exclude air. It dissolves easily and practically completely in warm water, in the proportion of 100 g of solids to 300 ml of water. It is very easily oxidized by

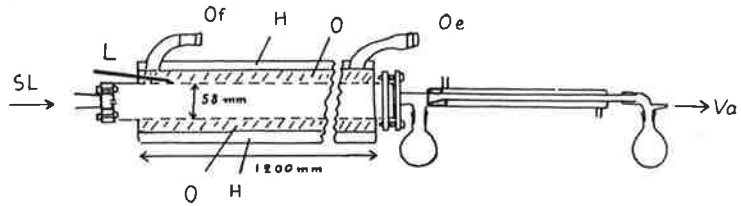


Fig. 1. Reactor tube for demethylation of kraft black liquor at atmospheric or reduced pressure. Volume 3 l. SL — inlet of spent liquor. O — oil in mantle. H — electric heating. Of — tube for filling of oil. Oe — tube for emptying of oil. Va — suction for vacuum. L — thermometer.

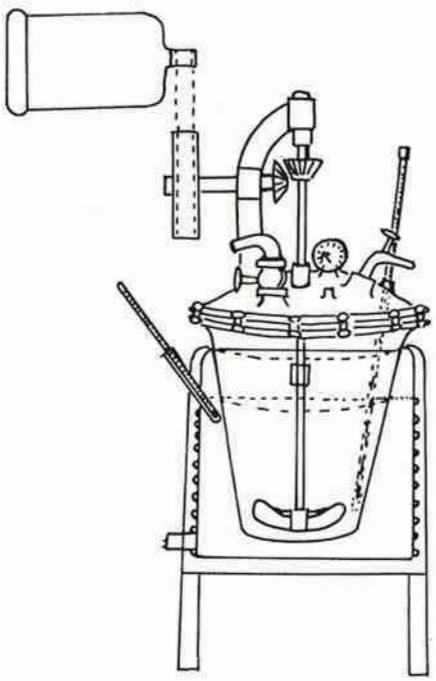


Fig. 2. Reaction vessel for demethylation of kraft black liquor at atmospheric or reduced pressure. Volume 12 l.

the oxygen of air. If the solid is brought as hot into contact with air, a strong exothermic oxidation takes place, the matter begins to glow, and carbonizes. During experiments, suction of air into the hot reaction mixture, for instance through leaks in the apparature, must be strictly avoided.

Fig. 2 shows a 12 l reaction vessel, originally designed for lacquer cooking in the paint industry, which we have used for demethylation of kraft black liquor. In the first experiments, it was heated directly with electric resistance elements, later indirectly in an oil bath. Also here, the reaction mixture was slowly sprayed into the hot vessel, in this case using mechanical stirring.

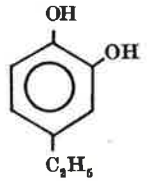
During heating with alkali, the reaction mixture at first is in a fluid state, being dark brown and glittering like silk, and still easy to mix, until the temperature has attained about 160°C. The main part of the water distils off at that preliminary stage. At about 160—200° the mixture solidifies, assumes a yellowish light brown color and swells suddenly, in a way similar to rising dough for breadbaking. Because of this swelling, the reaction vessel for every kg of kraft black liquor of about 50 % solids content must have a space of at least 3 liters, if diminished pressure is used, and 6 l at common pressure. During the swelling, the reaction mixture becomes hard, usually causing the mechanic stirrer to stop. At maximum temperature, about 300°C, the substance is dark and thacky, adhering strongly to transport screws etc., thus being difficult to move from one vessel to another. At cooling it gives a brittle solid.

Results of demethylation at common or reduced pressure.

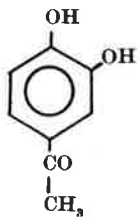
Compared with the results of pressure heating of black liquor in autoclaves [4,6] the demethylation at common or reduced pressure seems to go farther, especially giving substantial yields of oxalic acid and, in addition, yields of acetic and formic acid, which are about twice the amounts of these acids in original black liquor, and about 1 1/2 times as great as the yields at pressure heatings. Further, the presence of added sodium sulfide or mercaptide seems to be deleterious at common or diminished pressure, in contrast to its advantageous effect in pressure heatings. At common or diminished pressure addition of sulfide or mercaptide during demethylation leads to the formation of dark and resinous matter, insoluble in ether. The best results were obtained at addition of sodium hydroxide alone. It seems, that on demethylation at common or reduced pressure the concentration of the alkaline reagents becomes so high, that reactions easily go too far if the strongly nucleophilic sulfidic reagents are used (cf [28]).

Table 1 shows some results of heatings of commercial kraft black liquor from the mill of Enso-Gutzeit, Kotka, after addition of alkali. The black liquor had solids content 51.9 %, ash content 21.1 %, and content of organic matter calculated as 1.353 × loss at ignition 41.7 %. The factor 1.353 is derived from experiments and considerations of the usual composition of black liquor. After demethylation, the solid residue was analysed using a simplified procedure, whereby the matter was dissolved in water, precipitated with hydrochloric acid and filtered, the precipitate being washed with hot water. The filtrate and the precipitate were both extracted thoroughly with ether, and the filtrate thereafter also with ethyl methyl ketone. The ether insoluble part of the precipitate is designed as "demethylated lignin" (DL) in Table 1.

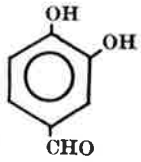
Oxalic acid seems to be formed on heating of kraft black liquor with alkali at common pressure beginning already from about 200°C upwards. This acid was determined by analyses in a separate part of the filtrate before extraction with ether by precipitation with calcium chloride solution after addition of ammonia, and dissolution of the precipitate in warm 2 N



IV. 4-ethylcatechol



V. 4-acetopyrocatechol



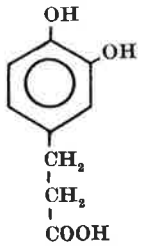
VI. Protocatechualdehyde

sulfuric acid and titration with 0.1 N potassium permanganate solution. Acetic and formic acids were determined in separate portions of the reaction mixture according to [4]. The different analyses were carried out by phil.cand.:s *Harriet Björnström* and *Eva Solin*.

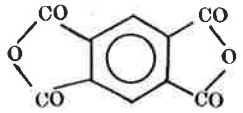
The most interesting fraction obtained was the ether and water soluble, non volatile (EWS) one. The yield of it gives a measure of how far the demethylating degradation has gone. By separate determinations it was found that about one third of this fraction consists of phenols, especially *pyrocatechol* (XI) and further its homologues, i.a. *4 methyl-* and *4 ethyl-catechol* (XIII and IV), as well as some *4-acetopyrocatechol* (V) and *protocatechualdehyde* (VI), the pyrocatechol dominating. This fraction crystallizes on standing, even without distillation or sublimation, provided it is carefully washed free from acids with sodium hydrogen carbonate solution. Recrystallization once from benzene gives practically pure, crystalline pyrocatechol, all the homologues being left in the mother liquor.

About two thirds of EWS consists of acids, separated from the phenols by shaking with sodium hydrogen carbonate solution. As pyrocatechol and its derivatives are more or less easily soluble in water, the sodium hydrogen carbonate layer was thoroughly shaken with ether, 5 times, in order to remove the phenols. Among the acids, phenol carboxylic acids dominate. Among them is some *protocatechuic acid*, (XV) but probably more *homoprotocatechuic* (cf [24]) (XII) and *dihydrocaffeic* acids (VII). In addition there occur, considerable amounts of *succinic acid*, identified by mixed melting point and infrared spectrum. Further, chromatography indicated small amounts of homologues of succinic acid, namely glutaric, adipic, pimelic, suberic, azelaic, and sebacic acids. These acids were chromatographed by *G. Nordman*, on silica (Kieselgel), first in a column and then on thin layers.

The ether soluble, in water insoluble fraction (ES) is often the largest. It contains some tall oil constituents, soluble in petrol ether or kerosene — the main part of them had been separated already in the mill as crude soap. Most of ES seems



VII. Dihydrocaffeic acid



VIII. Pyromellitic acid anhydride

to consist of semisolid, rather far degraded demethylation products of lignin. Perhaps its most interesting property is that it can be cracked to pyrocatechol and other phenols.

The "demethylated lignin" (DL), is insoluble in ether as well as in water. It is also a kind of degraded lignin, which is practically totally soluble in ethyl methyl ketone or in alcohol, in contrast to original kraft lignin. The yield of DL is lower the better the degradation reaction has succeeded, going down to about 5 % at the best degradations. This substance is dark and brittle. It seems to be difficult to crack to low molecular phenols. Because it probably contains pyrocatechol groups it could possibly find use for absorption of oxygen in alkaline solution. *G. Brunow* has investigated samples of similar preparates obtained at pressure demethylation, oxidizing them with potassium permanganate and nitric acid [29], cf [30-33]. He found that it gave benzene penta- and hexacarboxylic acid (mellitic acid), from which pyromellitic acid anhydride (VIII) can easily be made through dry distillation. VIII is valuable for making plastics of high melting point [34], but the yield of it from the demethylated lignin was low, about 3 % only.

Table 1. Heating of kraft black liquor samples (720 g, 51.9 % solids) with alkalies in 3 liter oil mantle tube, 60 min., about 30 mm. All %:ages calculated on organic matter of liquor.

Number of heating	921	939	978	967	988	995
°C in oil mantle	286 [1]	285	300 [1]	300	300	300
% NaOH added	25	25	30	40	33	30
% Na_2S added	15.9	15.9	3.5	—	—	—
Demethylat. lignin (DL)	12.7	20.5	14.5	5.2	9.3	15.7
Sol.in ether and water (EMS) [2]	17.5	13.7	23.9	23.4	24.1	18.9
Sol.in ether, ins.in water (ES) [3]	27.6	24.0	24.7	29.8	32.9	31.4
Acetic acid	10.8	10.0	11.2	9.2	10.9	
Formic acid	9.4	11.0	11.2	10.5	10.8	
Oxalic acid	16.6 [4]	15.6 [4]	13.8 [5]	19.5 [5]	18.5 [5]	19.6 [5]

1. Live steam was used. 2. Pyrocatechol + homoprot.acid + homologues and some carbonyl derivatives. 3. To be cracked. 4. Titrimetrically. 5. Total fraction soluble in butanone after extraction with ether.

Table 1 shows among other things that addition of sodium hydroxide in an amount of about 33 % of the organic matter suffices to give good yields of the ether soluble fractions, and that substitution of sodium hydroxide by sodium sulfide decreases the yields of these fractions and increases the yield of demethylated lignin.

Table 2. Heatings of different spent liquor matters with alkalies. Yields and NaOH additions as % of organic matter.

No of heating	999	1002	1007	1019	1046	1051
Starting material	Softwood kraft black liquor		Birch kr. black liq.	Softwood kraft lignin	Skutskär sulfite [1]	Rauma
Volume of reaction vessel, liters	12	12	3	3	0.7	0.7
°C	300	300	290	290	325	325
Time at maxim. temperature, min.	60	60	60	60	30	30
Pressure, mm Hg	130	130	72	122	760 [1]	760 [2]
Added NaOH, %	33.3	33.3	35	70	131	110
Yields, %:						
Demethylated lignin (DL)	6.6	5.7	12.4	15.4	9.0	10.4
Sol. in ether and in water (EWS)[3]	24.4	24.6	18.9	19.5	20.3	13.8
Sol. in ether, insol. in water (ES)[4]	31.5	36.7	20.2	26.5	33.1	27.5
Soluble in butanone[5]	17.1	13.7	9.2 [6]	4.1 [7]	7.6 [7]	4.0

1. Live steam was introduced in reaction mixture. 2. Current of nitrogen. 3. Pyrocatechol, homoprotocatechuic acid + homologues and some carbonyl derivatives. 4. To be cracked. 5. After extraction with ether. 6. Acetic acid 14.4 %, formic acid 3.2 %. 7. Contained oxalic acid.

Table 2 shows that heating in the 12 liter kettle gives even better yields of the most significant ether soluble fractions than the heating in the reactor tube. Corresponding heatings of commercial birch kraft black liquor from the mill of Kuusankoski (exp. 1007) shows degradation, but not as good results as demethylation of the usual pine kraft black liquor. Dr *W. Forsman* has studied the demethylation of birch kraft black liquors and found strong chromatographic indications that they, in addition to pyrocatechol and its derivatives, also, as could be expected, contain pyrogallol and its derivatives, i.a. syringic acid. In addition, i.a. vanillic and α-resorcinic acid, as well as resorcinol were indicated in small yields.

Heating of isolated kraft lignin (exp. 1019) does not give better yields of ether soluble fractions than original kraft black liquor, and the yield of oxalic acid is low. Thus, it seems to be of considerable advantage not to isolate the lignin, but heat the

whole kraft black liquor with alkali. Sodium base sulfite liquor from Skutskär, using the Stora process (exp. 1046), and Rauma, using the Sivola process (exp. 1051), can be demethylated, but need addition of sodium hydroxide in high amounts, probably in order to desulfonate the lignosulfonic acids. Also calcium base sulfite liquors (Table 3) can be demethylated, but the

Table 3. Heating of commercial calcium base, not fermented sulfite spent liquor with alkalies.

Pressure 35—40 mm, reaction vessel 0.7 liter, 30 minutes at maxim.temp.

No of heating	1052	1053	1057	1056 [2]
Added NaOH, % [3]	82	77	49	73.3
°C	322	320	320	328
Yields, %:[3]				
Demethylated lignin (DL)	5.4	13.5	46.2	7.9
Sol. in ether and in water (EWS)	18.8 [4]	18.2	7.7	26.7
Sol. in ether, insol. in water (ES) [5]	37.3	34.9	22.3	26.3
Soluble in butanone [6]	7.2	6.7	6.2	6.5
Acetic acid	12.9	9.6		
Formic acid	1.9	1.0		

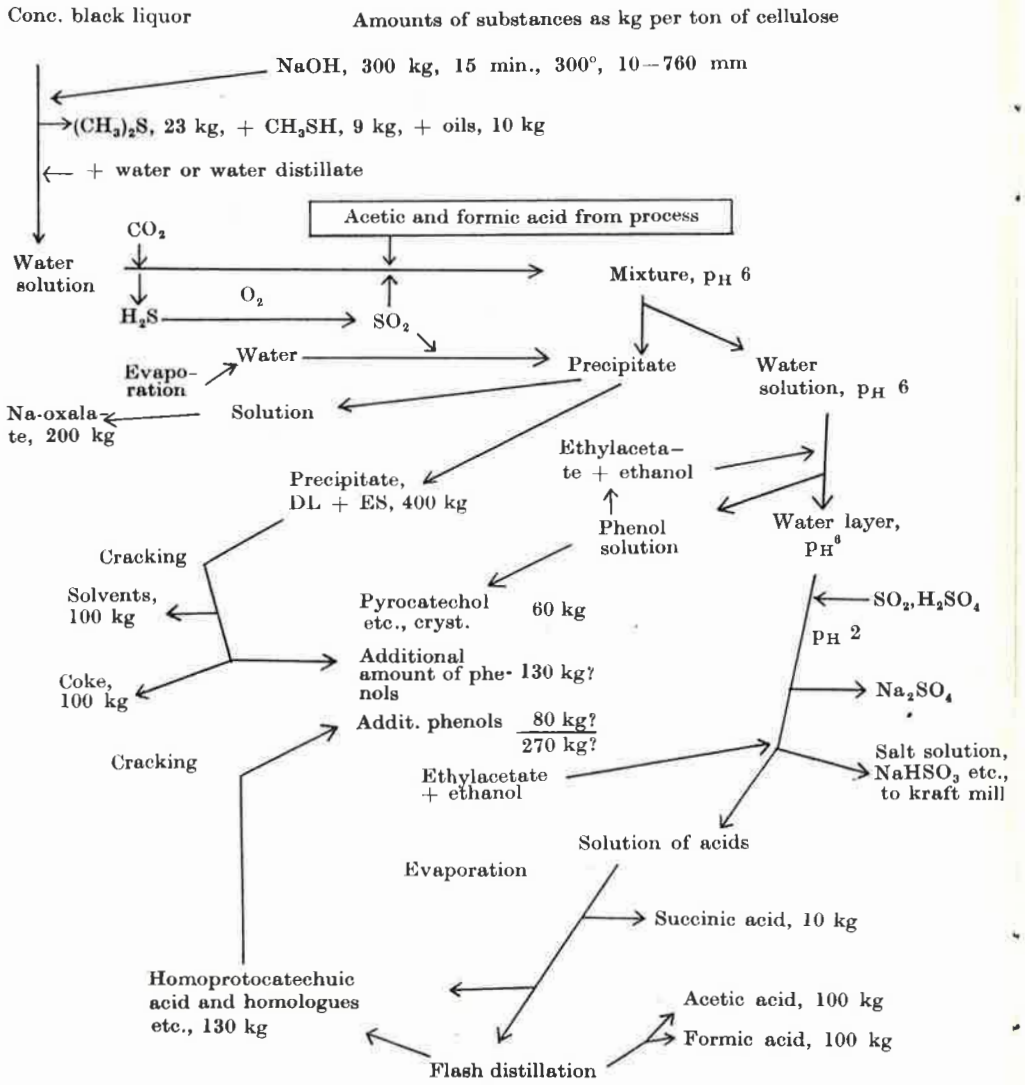
1. Spruce liquor from the mill of Kymmene, solids content 50.3 %, ash content 4.7 %, organic matter as difference 45.6 %. 2. Half kraft black liquor of the composition related in Table 1 and on p. 3, the other half was spent sulfite liquor of the kind mentioned in note 1. 3. Of the organic matter. 4. 6 % phenols, 12.8 % acids (non volatile). 5. To be cracked. 6. After extraction with ether.

amounts of sodium hydroxide added must be large, about 80 % of the organic matter, and the yields of oxalic and formic acids are low.

Separation of products.

Special attention has been paid to attempts to work out simple methods to separate the reaction products. The work in this direction is still continued. Scheme 1 contains a review of some main features of the proposed separation methods. The yields given are as yet only approximative.

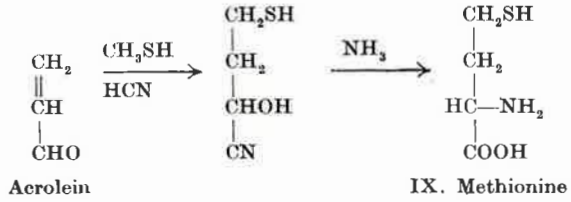
Scheme 1. Separation of products from demethylation of kraft black liquor.



During the heating with alkali, certain amounts of dimethyl sulfide and methyl mercaptan are evolved. These can be recovered rather easily. The yields of dimethyl sulfide are somewhat lower than in pressure heatings of kraft black liquor with additional sodium sulfide, or sodium hydroxide and sulfur, as it is practised in the industry [35]. Instead, my coworkers and I have found that by varying the temperatures and the added

amounts of sodium and sodium hydroxide, the process can be directed to give alternatively high yields of dimethyl sulfide or almost theoretical yields of methyl mercaptan, up to 90 kgs per ton of pulp. The dimethyl sulfide can be used for manufacture of dimethyl sulfoxide, as shown by *T. Smedslund* [36], cf also [37]. Methyl mercaptan has been utilized for manufacture of methionine (IX), starting from acrolein [38], as shown by the following abbreviated reaction scheme 2:

Scheme 2.



Methionine is said to be used as addition to fodder yeast to provide the necessary addition of sulfur containing amino acid to chicken feed.

In addition to dimethyl sulfide and methyl mercaptan, other volatile products are also obtained and distilled off together with water during the alkali heating of kraft black liquor. These products are being studied by *Ö. Wahlroos*. In this water distillate small amounts of an oil separates. It contains phenols, among which i.a. phenol, cresols and guaiacol are indicated by chromatography, but also other substances, among them bases, whose odor remembers that of pyridin and other bases in coal tar or Dippel oil. They probably originate from proteins in the wood used for pulping.

These phenols and other substances could probably be enriched by recycling, which here means using the water distillate from an alkali heating for dissolution of the reaction product and the added alkali in a later heating.

An important step on separation of the reaction products is the neutralization of the alkaline solution of the reaction product to about p_H 6. This can be performed by use of carbon dioxide, sulfur dioxide, sulfuric acid or acetic and formic acids from an earlier batch of the process itself. Carbon dioxide, as well as the other acidics, evolves hydrogen sulfide, which can be burnt to sulfur dioxide. Neutralization with sulfur dioxide is of advantage, because it to some extent protects the pyrocatechol against autoxidation. Pyrocatechol and its derivatives in alkaline solution or as lead salts are oxidized very fast by

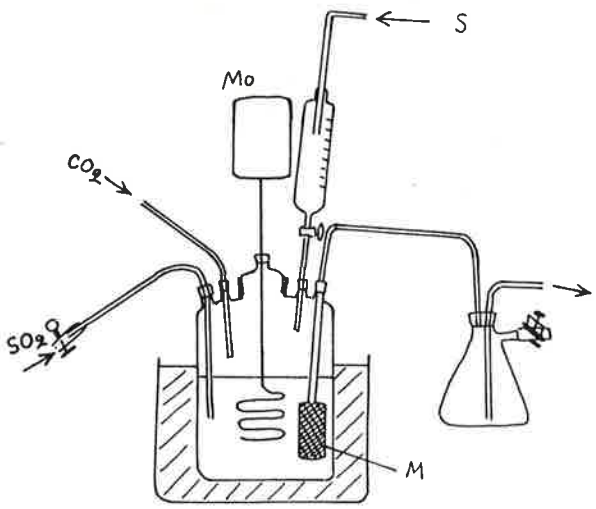


Fig. 3. Four neck glass apparatus for neutralization and decantation of water solution of demethylation product of kraft black liquor. S — inlet for water solution of demethylation product. M — metal wire net for inverse filtration. Mo — electric motor for stirrer.

the oxygen of the air. Hence, the procedure must be such that air is excluded, which is easier to achieve in a mill than in the laboratory. As sulfur dioxide reacts with hydrogen sulfide forming elemental sulfur, it seems to be best to remove the hydrogen sulfide before sulfur dioxide is introduced.

At p_H 6 a precipitate is formed, which can be easily separated by decantation. In the laboratory this has been performed at about 60° in the simple apparatus shown in Fig. 3. The filtrate can be separated by decantation or a kind of inverse filtration through a metal net of the same kind as that in the paper industry for fiber filtration. The precipitate is thus very much easier to separate than for instance lignin precipitated by acidification of black liquor.

The precipitate obtained at p_H 6 consists of demethylated lignin (DL), matter soluble in ether, but not in water (ES), and big amounts of sodium oxalate. This salt can be easily extracted from the precipitate with hot water, from which it also can be recrystallized, the solubilities of the neutral and acidic sodium oxalates in g per 100g of water being as follows [39]:

°C	$(COONa)_2$	COOH COONa
15.5	3.23	1.66
100	6.67	21.3

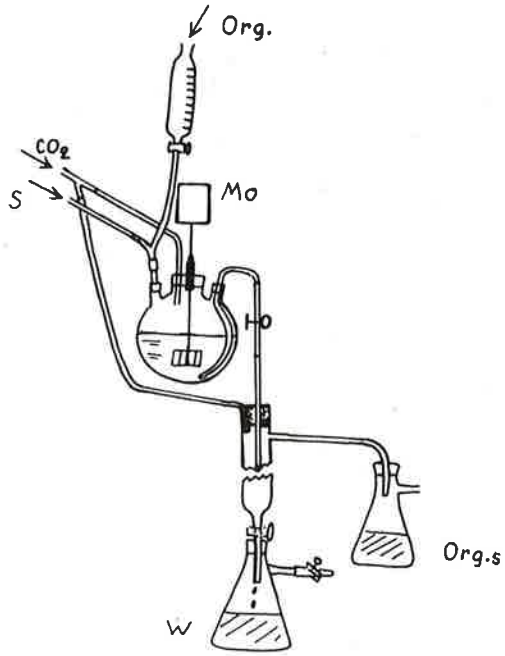


Fig. 4. Glass apparatus for continuous extraction with organic solvent. Mo — electric motor for stirring. Org — intake of organic solvent. S — inlet for water solution of reaction products. W — extracted water layer. Org s — solution of phenols or acids in organic solvent.

Recrystallization thus is easier with the acidic oxalate than with the neutral, and the extraction of the precipitate is best made with an acidic solution such as dilute sulfuric or strong sulfurous acid. The acidic filtrate from the acid sodium oxalate can be used in later stages of the process for acidification.

The filtrate of p_H 6 has to be adjusted to a somewhat higher p_H, at least 7. This can be made by addition of white or green liquor or other alkalies or, in cases where the filtrate contains sodium hydrogen carbonate, by heating, which causes evolution of carbon dioxide. The solution is then extracted with an organic solvent such as butanone (ethyl methyl ketone) or a mixture of 7 volumes of ethyl acetate with 3 volumes of ethanol. This mixed solvent has the advantage that it can be manufactured from sulfite alcohol and acetic acid obtained from the process itself. The extraction can be made continously in the simple laboratory apparatus shown in Fig. 4.

From the extract obtained at about p_H 7 the solvent is evaporated. The residue can be recrystallized from benzene

(cf p. 6). Thus this extract can be divided into pure catechol and catechol homologues plus carbonyl derivatives.

The following step will be acidification of the p_H 7 water layer to about p_H 2, which can be made by use of sulfur dioxide and some sulfuric acid or sodium hydrogen sulfate. A new extraction with butanone or ethyl acetate-ethanol isolates the acids. Evaporation of part of the solvent causes succinic acid to crystallize in a yield of about 1 % of the organic matter; the mother liquor still contains some succinic acid. This crystallization takes place more easily if the solution has been purified by use of for instance active carbon. The succinic acid can be filtered or centrifuged off and recrystallized from hot water.

The best way to isolate the protocatechuic acid and its homologues is still studied. It seems that fractionated crystallization by further evaporation of the solvent from the filtrate after isolation of the succinic acid will be possible.

The continuation of the separation procedure resembles in principle the isolation of acetic and formic acids in the process used by Sonoco for neutral sulfite semichemical spent liquor ([40]): distillation off of solvent, flash distillation, combined with separation of acetic and formic acids by azeotropic distillation with ethylene dichloride, and collection of less volatile products as flash distillation residue.

Cracking of some fractions.

The matter of the precipitate obtained at p_H 6 represents even after removing of the sodium oxalate by extraction with hot water still about 40 % of the organic matter of the original kraft liquor, of which roughly 3/4, or 30 % of the organic matter mentioned, is soluble in ether (fraction ES). Possible uses of this matter have been studied in various ways. For the moment the most promising way to use it seems to be to crack it during a very short time, about one second, at 500—1000° at atmospheric pressure or at about 350—500° in vacuum, in a current of nonreactive gas such as carbon dioxide or nitrogen (cf cracking of various phenols [41]). Chomatograms of the cracking products show presence of pyrocatechol and its homologues and several phenolic substances with high R_f values in the xylene-butanone-formamide paper chromatographic system of Freudenberg and Lehmann [42], probably monovalent phenols. Thus the ES seems to give very much the same products upon cracking as those obtained as distillates at the first stage of heating with alkali (p. 11).

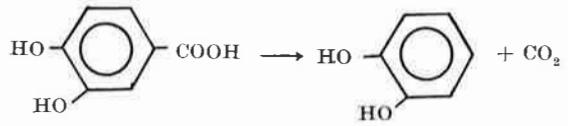
This cracking process is still further studied. In the best experiments only small amounts, 30 % or less, of carbon or coke are formed, provided that the cracking is carried out

on the ether soluble matter ES only. The simplest way to separate the ether insoluble demethylated lignin (DL) from ES as yet found is to dissolve the mixture in butanone and precipitate the DL by addition of the same volume of toluene or ligroin.

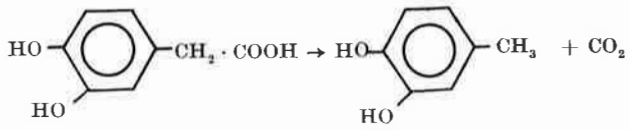
Possibly part of the cracking products could be used as solvents for the extraction of the black liquors.

Protocatechuic acid has been proposed for use as starting materials for synthetic fibers [43]. Probably its homologues could be used also in the same way. Another use for them would be cracking, especially in presence of copper or sodium carbonate (studies made by *K. Penttinen* and *R. Stabel-Taucher*) to give the corresponding catechol homologues by decarboxylation:

Scheme 3.



X. Protocatechuic acid XI. Pyrocatechol



XII. Homoprotocatechuic acid XIII. 4-Methyl catechol

In this way the yields of catechols would be still further increased.

Outline for plant arrangement.

An outline to the total arrangement of a future plant for the processing of kraft black liquor is given in figure 5. As the reaction mixture heated at common or diminished pressure is difficult to move from one vessel to another, the process is planned as a semicontinuous procedure, with several reaction vessels parallelly arraigned, with common inlet and outlet for chemicals. In each vessel the following stages are performed: spraying in, evaporation, rising of temperature to maximum, heating 15—30 min. at maximum, cooling down, dissolving in hot water or water distillate from an earlier charge, and emptying. The heating is planned to be performed by introduc-

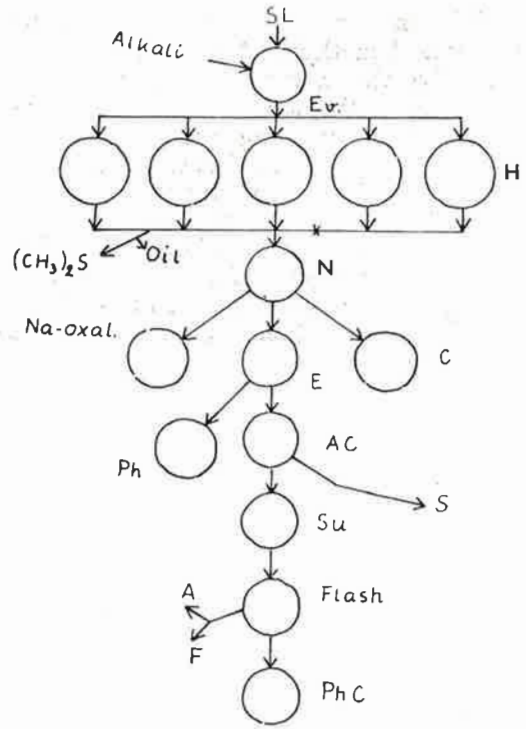


Fig. 5. Schematic outline for arrangement of demethylation plant. SL — intake of spent liquor. Ev — further evaporation. N — neutralization, decantation, extraction of precipitate with hot, dilute acidic water. Na-oxal — crystallization of (acid) sodium oxalate. C — cracking. E — continuous extraction with ethyl acetate-ethanol. Ph — crystallization of phenols. AC — acidification to pH about 2. S — inorganic salt solution, to kraft mill evaporation. Su — succinic acid crystallization. Flash — flash distillation. A — acetic acid. F — formic acid. Ph C — phenol carboxylic acids. These can perhaps at least in part be obtained as crystalline precipitates already before flash distillation.

tion of heating oil in coils led in tubular helixes through the reaction mixture. Experiments with this are going on. The oil flowing through the coils will be heated outside in a calorisator. The cooling down will be performed so that the hot oil will be emptied from the coil and led into the heating coils in other vessels. Thus, instead of the difficultly moved reaction mixture the heating oil will be moved in the apparature. The whole arrangement is similar to the set up in a batchwise operating pulping plant. In the real plant, the "parallel" vessels can be arraigned in a circle, the same as the digesters in a pulping plant.

Yield and value of the products.

The yields given in the schemes 1 and in the Table 4 are calculated supposing that the cracking operations are fully developed, which is not yet the case. However, the numbers in Table 4 give some idea of the amounts and nature of the

Table 4. Organic chemicals per ton of cellulose.

	kg	mk
Pyrocatechol and other 2-valent phenols	140	203
Phenol and other monovalent phenols	130	107
Oxalic acid	150	198
Acetic acid	100	66
Formic acid	100	109
Succinic acid	10	40
Solvents and other oils	130	26
Dimethylsulfide	30	30
Coke?	100	5
Sum	890	784

products expected. The values given in Table 4 to right are given as world market prices, so far as these can be established [49]. Their sum is about 2 times the value of the cellulose (unbleached kraft pulp calculated as worth 350 finnish marks or 109 dollars per ton). The determining thing of course will be whether the products really can be mass produced and sold for the prices estimated. It is, however, very possible, that further research will result in new and still more valuable products.

The alkali heating and the separation of products of course costs something. However, the alkalies can be regenerated and the isolation methods after all are simple, for each chemical not much more complex than the isolation and further processing of tall oil.

The fuel value of the black liquor must also be considered. However, the treatment on the lines of the scheme 1, and especially the extractions with solvents, have been found to give tar like byproducts, as well as coke from the crackings, which certainly will be possible to use as water free fuel materials. If more fuel is needed, parts of the demethylated lignin or the ES-fraction can be burnt.

Thus, the net costs of the separation of chemicals probably will not be very high.

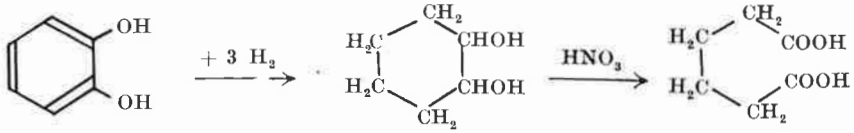
Of the different products, oxalic acid is used by now in amounts of about 200 tons per year in Finland and about 10 000 tons per year in the U.S.A. Thus, the black liquor from one big kraft mill could give oxalic acid in yield of an order of magnitude of the present world consumption. New uses for oxalic acid

thus would be desirable. Oxalic acid can probably be used for easy manufacture of pure formic acid, not to speak of carbon monoxide, carbon dioxide or hydrogen. It can be substituted to oxalyl chloride, which could be used for manufacture of polycarbonate resins. Oxalic acid can also be used as an acidic condensation reagent for i.a. phenol-formaldehyde plastics. In this respect it has some special advantages, because it has bleaching properties and in fact gives rather light colored products, for instance from pyrocatechol and formaldehyde, which give dark products in alkaline solution. Also at condensation with sulfuric or toluenesulfonic acids they give darker products than with oxalic acid. Further, oxalic acid is one of the few chemicals possible to be produced in big amounts, which precipitate sodium ions from comparatively diluted neutral or even acidic solutions. The remaining excess of oxalic acid can be removed easily by precipitation as calcium salt. Oxalic acid could thus perhaps be of use for regeneration of sodium chemicals.

The acetic and formic acid acquired from the Sonoco process already mentioned are said to make this process profitable, together with the sodium sulfate formed (salt cake) from the sulfuric acid added. Recently, Weyerhauser has spent about one mission dollars to develop a process for isolating acetic acid from sulfite pulping spent liquor [44]. It should also be possible to manufacture acetaldehyde from the roughly equal amounts of formic and acetic acid formed from demethylated kraft black liquors. This would give the kraft mills the opportunity to manufacture most of the chemicals which by now can be made from the alcohol produced in the sulfite pulping industry.

Pyrocatechol is known to be a very effective, tetrafunctional phenol for condensation with formaldehyde to bakelite type plastics. It is so effective, that it can be mixed 50:50 to for instance guaiacol or other weakly reacting phenolics and still give a quite reactive starting material for bakelite.[45] Probably an admixture of pyrocatechol to kraft lignin would give a satisfactory plastic. Pyrocatechol can also be hydrogenated to cyclohexanediol, which can be oxidized with nitric acid to adipic acid, the well known starting material for manufacture of nylon fibers [46] (scheme 4):

Scheme 4.



XI. Pyrocatechol — 1,2-cyclohexanediol — Adipic acid

Pyrocatechol and its homologues are formed on the pressure hydrogenation of isolated lignin in the Noguchi-Oshima process [48]. It is somewhat surprising, that the possibility to manufacture pyrocatechol is not mentioned in the recent report about the trial of the Noguchi-Oshima process by Crown and Zellerbach [47]. This process gives in part the same phenolics as the process outlined in the present paper. The difference is, however, that the process outlined here uses the whole black liquor, without isolating the lignin, and common or reduced pressure and easily regenerated alkalies instead of high pressure catalytic hydrogenation. The procedure suggested in the present paper also gives valuable byproducts, viz. dimethyl sulfide, and oxalic, succinic, acetic and formic acids. A drawback is perhaps that the process comprises a number of steps and treatments, if all products are to be isolated. From an economic point of view, it probably would be of advantage to use a shortened procedure, with taking out of some products only. Since the procedures are simple, and the same apparatus, for instance that for extraction and distillation of solvents, probably could be used for isolation of various products, the process should be very flexible and easily adapted after changing coniunctures. Clearly, a considerable amount of further research is needed for development of all the possibilities for the alkali heating process of spent liquors. It seems, however, already by now evident, that this procedure offers an important opening for the utilization of these liquors, which sooner or later will be applied on a considerable scale and is well worth while for further investigation.

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Viscosities, Densities and Related Properties of Binary Mixtures Containing Dimethyl Sulphoxide and Mono-Substituted Benzenes or Guaiacol

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The viscosities and densities at 25°, 35° and 45°C of the binary systems dimethyl sulphoxide- nitrobenzene, -benzaldehyde, -chlorobenzene, -toluene, -aniline, -phenol and -guaiacol have been determined. Excess molar volumes, rheochors and enthalpies of viscous flow have been calculated. The results have been discussed in terms of polarity and hydrogen bonding effects. A linear relationship is observed between polarity parameters (group moment, dipole moment and Hammett σ-function) and maximum (minimum) excess molar volumes.

As a continuation of our work concerning the viscosimetric and related properties of binary mixtures containing dimethyl sulphoxide [1] the present report deals with data for mixtures containing mono-substituted benzenes or guaiacol as the second component. Thus, the densities and viscosities at 25°, 35° and 45°C have been recorded for the following systems in the whole concentration range: Dimethyl sulphoxide (DMSO)-toluene (I), -benzaldehyde (II), -chlorobenzene (III), -nitrobenzene (IV), -aniline (V), -phenol (VI) and -guaiacol (VII). In addition, the molar volumes, excess molar volumes, rheochors and enthalpies of viscous flow at 25°C have been calculated.

Experimental. The viscosities and densities were determined at 25°, 35° and 45°C using Ostwald viscometers and pycnometers in the manner previously described.[2] The infra-red spectra of the pure components and the mixtures were recorded by means of a Perkin-Elmer Model 237 grating spectrometer using 1.0 and 0.1 mm sodium chloride cells. The solvent absorption was, when necessary, compensated using a cell of variable thickness.

Reagents DMSO from Societé Petroles Nationales d'Aquitaine, France was purified by distillation *in vacuo* followed by repeated recrystallization until a melting point higher than 18.50°C was

reached. Reagent grade samples of the other compounds studied were purified by distillation either at normal pressure or *in vacuo:* collected fractions or melting points: toluene 110.5—111.0°C, benzaldehyde 179.5—184.0°C, chlorobenzene 131.5—132.0°C, aniline 183.5—185.0°C, phenol mp. 41.0°C, guaiacol mp. 28.0°C. The product obtained from the distillation of toluene was stored over sodium. In the case of aniline the distillation was made over zinc filings and the product was stored in the dark. Nitrobenzene was purified by a rapid distillation *in vacuo*. All compounds were used freshly after fractionation, purification and drying.

Results and Discussion. The results of the density and viscosity measurements and the calculated molar volumes at 25°C recalculated by graphic or numeric interpolation to whole tenths of molar fraction units are given in Tables 1—7 and Fig. 1. Owing to the difficulty of finding any empirical equation which, using only few parameters, could fit all the data with reasonable accuracy no such equation was calculated. The calculated rheochors and enthalpies of viscous flow at 25°C are collected in Table 8 as well as the excess molar volumes and excess rheochors [10] in Fig. 2 and 3 respectively.

Table 1. Densities, viscosities and molar volumes for the system DMSO-toluene (I) at 25°, 35° and 45°C.

x_{DMSO}	d_4^{25}	η_{25}	d_4^{35}	η_{35}	d_4^{45}	η_{45}	v_m^{25}
0.00	0.8616	0.549	0.8515	0.488	0.8417	0.442	106.86
.10	.8794	.606	.8687	.537	.8589	.482	103.17
.20	.8980	.675	.8866	.594	.8770	.530	99.48
.30	.9176	.761	.9059	.664	.8964	.587	95.83
.40	.9378	.867	.9262	.741	.9168	.654	92.27
.50	.9590	.990	.9481	.833	.9386	.731	88.77
.60	.9822	1.122	.9718	.937	.9621	.817	85.25
.70	1.0077	1.268	.9969	1.065	.9869	.921	81.70
.80	1.0343	1.452	1.0241	1.217	1.0142	1.047	78.25
.90	1.0639	1.679	1.0536	1.407	1.0439	1.201	74.75
1.00	1.0957	2.000	1.0857	1.659	1.0756	1.395	71.30

Table 2. Densities, viscosities and molar volumes for the system DMSO-benzaldehyde (II) at 25°, 35° and 45°C.

x_{DMSO}	d_4^{25}	η_{25}	d_4^{35}	η_{35}	d_4^{45}	η_{45}	v_m^{25}
0.00	1.0431	1.385	1.0333	1.178	1.0251	1.034	101.71
.10	1.0468	1.443	1.0369	1.220	1.0285	1.066	98.70
.20	1.0508	1.510	1.0407	1.266	1.0320	1.101	95.66
.30	1.0549	1.562	1.0448	1.314	1.0357	1.135	92.64
.40	1.0593	1.620	1.0491	1.362	1.0397	1.170	89.61
.50	1.0640	1.679	1.0538	1.411	1.0442	1.207	86.58
.60	1.0692	1.739	1.0591	1.461	1.0492	1.243	83.55
.70	1.0750	1.801	1.0648	1.510	1.0547	1.280	80.49
.80	1.0816	1.864	1.0710	1.560	1.0607	1.317	77.41
.90	1.0884	1.938	1.0788	1.609	1.0675	1.354	74.36
1.00	1.0957	2.000	1.0857	1.659	1.0756	1.395	71.30

Table 3. Densities, viscosities and molar volumes for the system DMSO-chlorobenzene (III) at 25°, 35° and 45°C.

x_{DMSO}	d_4^{25}	η_{25}	d_4^{35}	η_{35}	d_4^{45}	η_{45}	v_m^{25}
0.00	1.1015	0.755	1.0908	0.673	1.0798	0.607	102.19
.10	1.1015	.826	1.0909	.738	1.0798	.656	99.06
.20	1.1014	.905	1.0908	.807	1.0798	.709	95.95
.30	1.1011	.993	1.0906	.880	1.0796	.769	92.92
.40	1.1006	1.094	1.0901	.958	1.0793	.832	89.76
.50	1.1000	1.206	1.0896	1.043	1.0788	.902	86.67
.60	1.0992	1.329	1.0890	1.136	1.0783	.981	83.61
.70	1.0984	1.466	1.0882	1.239	1.0777	1.068	80.53
.80	1.0975	1.616	1.0874	1.361	1.0770	1.165	77.45
.90	1.0966	1.784	1.0865	1.500	1.0763	1.274	74.38
1.00	1.0957	2.000	1.0857	1.659	1.0756	1.395	71.30

Table 4. Densities, viscosities and molar volumes for the system DMSO-nitrobenzene (IV) at 25°, 35° and 45°C.

x_{DMSO}	d_4^{25}	η_{25}	d_4^{35}	η_{35}	d_4^{45}	η_{45}	v_m^{25}
0.00	1.1986	1.825	1.1889	1.553	1.1789	1.318	102.71
.10	1.1903	1.851	1.1803	1.569	1.1705	1.333	99.65
.20	1.1816	1.877	1.1716	1.586	1.1619	1.349	96.58
.30	1.1726	1.903	1.1626	1.605	1.1530	1.353	93.48
.40	1.1631	1.927	1.1532	1.623	1.1436	1.377	90.38
.50	1.1531	1.946	1.1431	1.639	1.1334	1.388	87.26
.60	1.1427	1.962	1.1327	1.653	1.1227	1.396	84.12
.70	1.1317	1.975	1.1215	1.662	1.1114	1.402	80.96
.80	1.1202	1.985	1.1099	1.665	1.0999	1.403	77.78
.90	1.1081	1.993	1.0979	1.664	1.0880	1.400	74.57
1.00	1.0957	2.000	1.0857	1.659	1.0756	1.395	71.30

Table 5. Densities, viscosities and molar volumes for the system DMSO-aniline (V) at 25°, 35° and 45°C.

x_{DMSO}	d_4^{25}	η_{25}	d_4^{35}	η_{35}	d_4^{45}	η_{45}	v_m^{25}
0.00	1.0183	3.708	1.0088	2.745	0.9998	2.113	91.45
.10	1.0271	3.830	1.0176	2.841	1.0086	2.194	89.20
.20	1.0359	3.940	1.0263	2.925	1.0172	2.259	87.00
.30	1.0445	3.990	1.0348	2.980	1.0255	2.300	84.85
.40	1.0526	3.938	1.0429	2.958	1.0336	2.294	82.77
.50	1.0604	3.756	1.0507	2.839	1.0413	2.232	80.75
.60	1.0677	3.445	1.0579	2.644	1.0485	2.106	78.79
.70	1.0749	3.055	1.0648	2.397	1.0554	1.938	76.87
.80	1.0818	2.664	1.0717	2.134	1.0621	1.746	74.99
.90	1.0889	2.313	1.0788	1.886	1.0688	1.529	73.13
1.00	1.0957	2.000	1.0857	1.659	1.0756	1.395	71.30

Table 6. Densities, viscosities and molar volumes for the system DMSO-pheno (VI) at 25°, 35° and 45°C.

x_{DMSO}	d_4^{25}	η_2^5	d_4^{35}	η_{35}	d_4^{45}	η_{45}	v_m^{25}
0.20	1.0812	8.913	1.0718	5.870	1.0633	4.150	84.09
.30	1.0844	7.767	1.0752	5.328	1.0662	3.888	83.77
.40	1.0866	6.467	1.0773	4.618	1.0683	3.486	80.73
.50	1.0879	5.173	1.0785	3.826	1.0694	2.977	79.16
.60	1.0888	4.111	1.0792	3.127	1.0702	2.489	77.63
.70	1.0901	3.282	1.0802	2.579	1.0710	2.090	76.07
.80	1.0918	2.726	1.0815	2.192	1.0720	1.794	75.86
.90	1.0937	2.308	1.0834	1.902	1.0735	1.577	72.90
1.00	1.0957	2.000	1.0857	1.659	1.0756	1.395	71.03

Table 7. Densities, viscosities and molar volumes for the system DMSO-guaiacol (VII) at 25°, 35° and 45°C.

x_{DMSO}	d_4^{25}	η_{25}	d_4^{35}	η_{35}	d_4^{45}	η_{45}	v_m^{25}
0.20	1.1388	10.62	1.1284	6.47	1.1192	4.35	100.92
.30	1.1404	12.40	1.1300	7.54	1.1208	5.01	96.75
.40	1.1391	11.90	1.1291	7.38	1.1199	4.98	92.82
.50	1.1352	9.46	1.1254	6.23	1.1161	4.40	89.09
.60	1.1296	6.91	1.1197	4.81	1.1104	3.59	85.46
.70	1.1226	4.97	1.1125	3.67	1.1032	2.80	81.89
.80	1.1144	3.59	1.1043	2.83	1.0948	2.20	78.73
.90	1.1054	2.66	1.0953	2.12	1.0856	1.75	74.84
1.00	1.0957	2.00	1.0857	1.66	1.0756	1.40	71.30

Table 8. Rheochors $[R]\eta$ according to Friend and Hargreaves [6] and enthalpies of viscous flow $\triangle H_v$ according to the Eyring equation [16] at 25°C for the binary systems investigated (I—VII).

x_{DMSO}	I	II	III	IV	V	VI	VII
	Rheochors $[R]\eta$ in cgs-units						
0.00	55.79	59.59	55.48	62.27	60.57	66	78
.20	53.28	56.64	53.29	58.76	58.07	62.16	76.25
.40	50.95	53.52	51.05	55.17	55.24	57.32	71.14
.60	48.54	50.34	48.58	51.46	51.72	52.09	61.19
.80	46.10	47.06	46.25	47.65	47.67	47.48	51.71
1.00	43.72	43.72	43.72	43.72	43.72	43.72	43.72
	Enthalpies of viscous flow $\triangle H_v$ in kcal/mole						
0.00	2.2	3.0	2.1	3.0	5.5	—	—
.20	2.3	3.2	2.1	3.1	5.4	7.6	9.0
.40	2.9	3.2	2.4	3.1	5.2	6.1	8.7
.60	(3.3)	3.2	2.9	3.1	4.8	5.0	6.6
.80	3.2	3.3	3.1	3.2	4.1	4.0	4.3
1.00	3.4	3.4	3.4	3.4	3.4	3.4	3.4

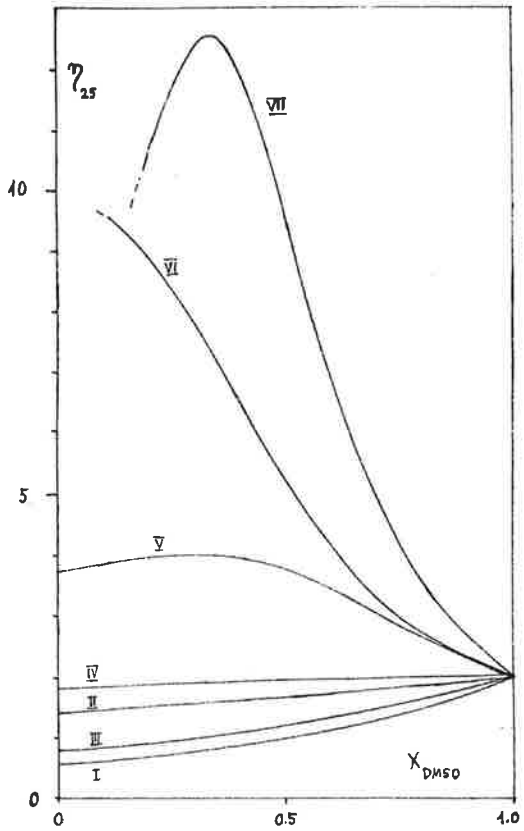

Fig. 1. Viscosities at 25°C in cP as a function of molar composition for the binary systems: DMSO-toluene (I), -benzaldehyde (II), -chlorobenzene (III), -nitrobenzene (IV), -aniline (V), -phenol (VI) and -guaiacol (VII).

The general hydrogen bond and association behaviour of the mixtures is readily deduced from the viscosity data plotted in Fig. 1. Thus, in those cases where a distinct intermolecular interaction between DMSO and the second component has been reported previously i.e. DMSO-aniline,[3] -phenol [4] and guaiacol [5] more or less marked maxima are observed in the viscosity and excess rheochor [10] (Fig. 3) curves. The very high maximum in the viscosity curve of the system DMSO-guaiacol indicates the transition from a weak intra-molecular to a strong intermolecular hydrogen bond formation [5] as the guaiacol content of the mixture is increased. In the case of DMSO-aniline and -guaiacol the maximum corresponds to a 1:2 composition of the mixture in molar units. However, this composition seems not to be in

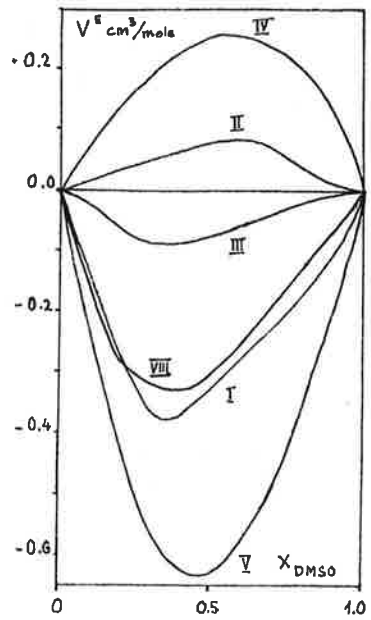

Fig. 2. Excess molar volumes V^E at 25°C for the binary systems investigated and DMSO-benzene. The values of (VIII) are recalculated from the density data in ref.[17] where V^E is given erroneously owing to a misprint. The numeration of the systems is the same as in the text and Fig. 1.

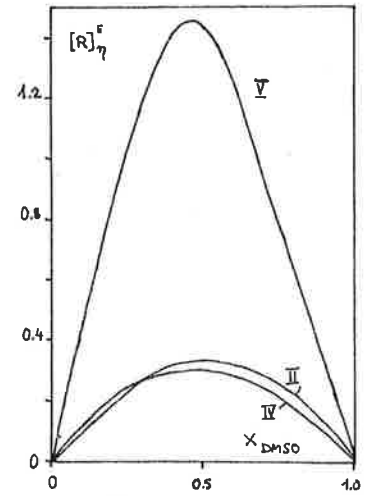

Fig. 3. Excess rheochors [10] $[R]^E_\eta$ in cgs-units at 25°C for the binary systems: DMSO-benzaldehyde (II), -nitrobenzene (IV) and -aniline (V).

agreement with the real stochiometry of the complexes formed. From experiments with thermal analysis,[3] the method of continuous variation,[3] infrared spectra [5] and also from the excess rheochor curve of DMSO-aniline in Fig. 3 it is expected to be of 1:1 type in the cases discussed. The reason for the discrepancy is obscure. In those cases where only a weak polar interaction between the components is to be expected as judged from infrared spectroscopic investigations, i.e. systems I—IV, only a weak deviation from linearity is observed in the viscosity and rheochor (not shown) curves.

In hydrogen bonded systems the molar volume is often smaller than an arithmetic average value calculated from the components [7,8] corresponding to a negative excess molar volume. It may be expected that the molar volume change follows the reverse pattern as heat of mixing i.e. the molar volume is increased as hydrogen bonds are broken and is becoming smaller as the bonds are formed. However, unexpected effects may occur. Thus, Migal and Belotskii [9] found that only slight indications of interactions could be detected by careful density and surface tension measurements of ethanol-aniline, whereas viscosity and refractive index data do not show a complex formation at all. In the ethanol-$CHCl_3$ system no interaction could be detected by these methods although an interaction is obvious from other observations.[8] It is of especial interest to note that also in the previously investigated systems DMSO-alcohols [1,10] and -sugars [11] a similar anomalous behaviour has been noted. Bearing in mind the possible presence of anomalies it is of interest to inspect the present molar volume data in the light of other physico-chemical information.

If the minimum (maximum) of the excess molar volume which is always observed in the $x_{DMSO} = 0.30-0.50$ range, is plotted against the group moment of the substituent group in the aromatic molecule [12] (plot not shown) or the dipole moment of the aromatic component (cf. Fig. 4) a nearly straight line is obtained. Unfortunately, owing to experimental difficulties, it was not possible to include the exact values for DMSO-phenol and -guaiacol in the plot. An even more linear relationship is obtained if the group or dipole moments are replaced by the Hammett σ-substituent reactivity constants (cf. Fig. 5 and the values reported in ref.[13]).

Recently Humffray, Ryan, Warren and Yung [19] presented the opinion that the "correct" value for the Hammett σ_p-constant of the formyl (CHO) group should be 0.45 instead of the generally accepted value 0.216.[13] The authors mentioned based their conclusions on measurements of acidity constants for iso- and tere-phtalaldehydic acid and also on other evidence. From Fig. 5 it is evident that the σ_p-value of the substituent in the aromatic

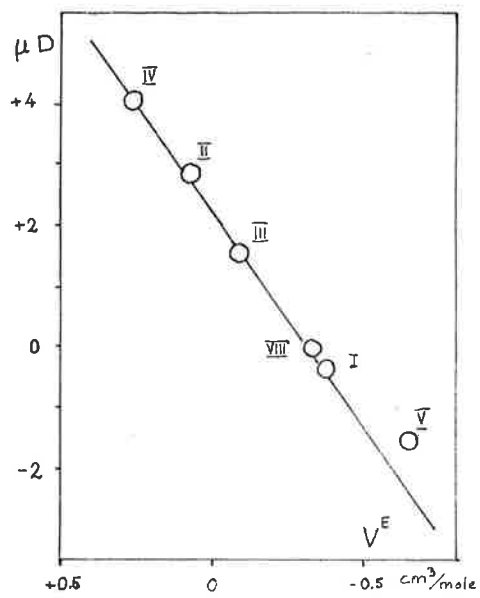

Fig. 4. Maximum (minimum) of the excess molar volume curve at 25°C as a function of the dipole moment of the aromatic component of the binary system including DMSO-benzene (VIII). The dipole orientation of toluene and aniline with respect to DMSO is assumed to be "opposite" to that of the other compounds given in the plot. The dipole moments are taken from ref.[18] and the numeration is the same as in Fig. 1 and in the text.

component of the binary system, in general, is a linear function of the maximum (or minimum) of V^E of the binary systems investigated. A distinct exception is, however, made by the benzaldehyde-DMSO system (II). From the straight line of the plot a σ_p-value of about 0.50 ± 0.05 can be deduced for the formyl group which is in accordance with the results of Humffray *et al.* As the volume change and dipole effect with certainty are caused by benzaldehyde the results obtained seem to support the use of the higher σ_p-value when considering the reactivity of aromatic compounds containing a formyl group in *para*-position to the reacting group.

From the results obtained the nature of the relation between intermolecular interaction and molar volume is evident. It is in accordance with the predictions made above and with the dipolar aprotic [14] and "nucleophilic" [15] nature of DMSO. As expected there seems further to be a continuous transition from unspecific intermolecular interaction to a directed association bonding when going from the system DMSO-nitrobenzene, DMSO-benzaldehyde etc. to DMSO-aniline and further to DMSO-phenols.

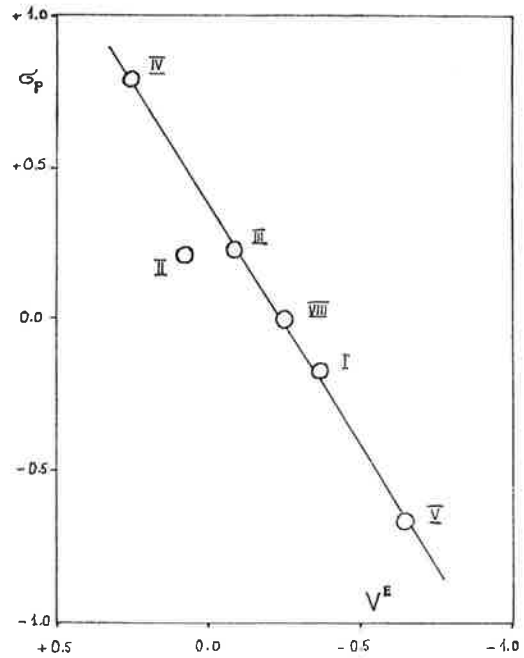

Fig. 5. Maximum (minimum) of the excess molar volume curve at 25°C as a function of the Hammett σ_p-constant for the substituent group of the aromatic component of the binary systems including DMSO-benzene (VIII). The σ_p-values are taken from ref.[18] and the numeration is the same as in Fig. 1 and in the text.

The enthalpy of viscous flow data given in Table 8 seem not to add any new information but to confirm the conclusions made.

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Finska Kemistsamfundets verksamhet

Protokoll fört vid Finska Kemistsamfundets möte 8.2.65 i TFiF:s lokal. Ordet fördes av docent *J. Johan Lindberg* med undertecknad *Saris* vid protokollet. Närvarande 45 personer.

§ 1. Ordföranden förklarade mötet öppnat och hälsade de närvarande välkomna. Han riktade sig särskilt till kvällens gästföredragshållare, tekn.dr *Karl N. Cederquist*, som inbjudits av Centralrådet för Finlands Kemister.

§ 2. Ordföranden höll ett minnestal över Samfundets hedersmedlem, doktor h.c. *Alfons Hellström*. Den avlidnes minne hyllades med en tyst minut.

§ 3. Årsberättelsen för år 1964 upplästes och godkändes. Under året har hedersmedlemmarna professor *Fredrik W. Klingstedt* och professor *Hans von Euler*, samt fil.mag. *Hans Sahlberg* avlidit. Deras minne hedrades med en tyst minut.

§ 4. Revisionsberättelsen upplästes.

§ 5. 1964 års styrelse och kassör beviljades ansvarsfrihet.

§ 6. Revisionsberättelsen för Centralrådets för Finlands Kemister för verksamhetsåret 1.11.63—31.10.64 upplästes. Dess bokslut och verksamhetsberättelse godkändes.

§ 7. Till Samfundets valda representant i Centralrådet utsågs docent *T.-M. Enari*. Samfundets ordförande är självskriven medlem av Centralrådet.

§ 8. Till medlemmar i Samfundet valdes fil.mag. *Jutta Aminoff* och fil.mag. *Henrik Tylli* på förslag av professor *Enkvist* och docent *Saris* samt dipl.ing. *Elisabet Mickos* på förslag av fil.mag. *Franciska Sundholm* och tekn.lic. *Göran Sundholm*.

§ 9. Tekn.dr *Karl N. Cederquist* (Stockholm) höll ett föredrag »Tekniska och ekonomiska synpunkter på våtförbränning av kloakslam». Diskussionsinlägg gjordes av dipl.ing. *H. Cajander*, prof. *Enkvist*, docent *Forsander*, mag. *Hallenberg*, mag. *S. Nordström*, ing. *Ingvar Olsson* (Stockholm), docent *Saris* samt dr *Tötterman*.

§ 10. Mötet avslutades med samkväm.

J. J. Lindberg *N.-E. Saris*

Protokoll fört vid Finska Kemistsamfundets ordinarie möte den 8 mars 1965 i TFiF:s lokal. Ordet leddes av ordföranden *J. J. Lindberg* med undertecknad *Saris* vid protokollet. Närvarande 12 medlemmar.

§ 1. Fil.dr *Johannes Turunen*, fil.mag. *Rolf Widlund* och fil.kand. *Corrado Majani* invaldes i Samfundet på förslag av prof. *Enkvist* och docent *Lindberg*.

§ 2. Bokslutet, årsberättelsen och revisionsberättelsen för Förlagsföreningen Acta Chem. Scand. föredrogs. Revisorn *W. Forsman* anmodades utreda frågan om placeringen av den summa med vilken Sverige avkortat Finlands tillgodohavande.

§ 3. Den av Sandoz producerade filmen »Oxytocin, die Geschichte eines Hormons» förevisades.

§ 4. Docent *Saris* höll ett föredrag »kalciumupptagning i intracellulära partiklar». Diskussionsinlägg gjordes av docent *Lindberg*.

J. J. Lindberg *N.-E. Saris*

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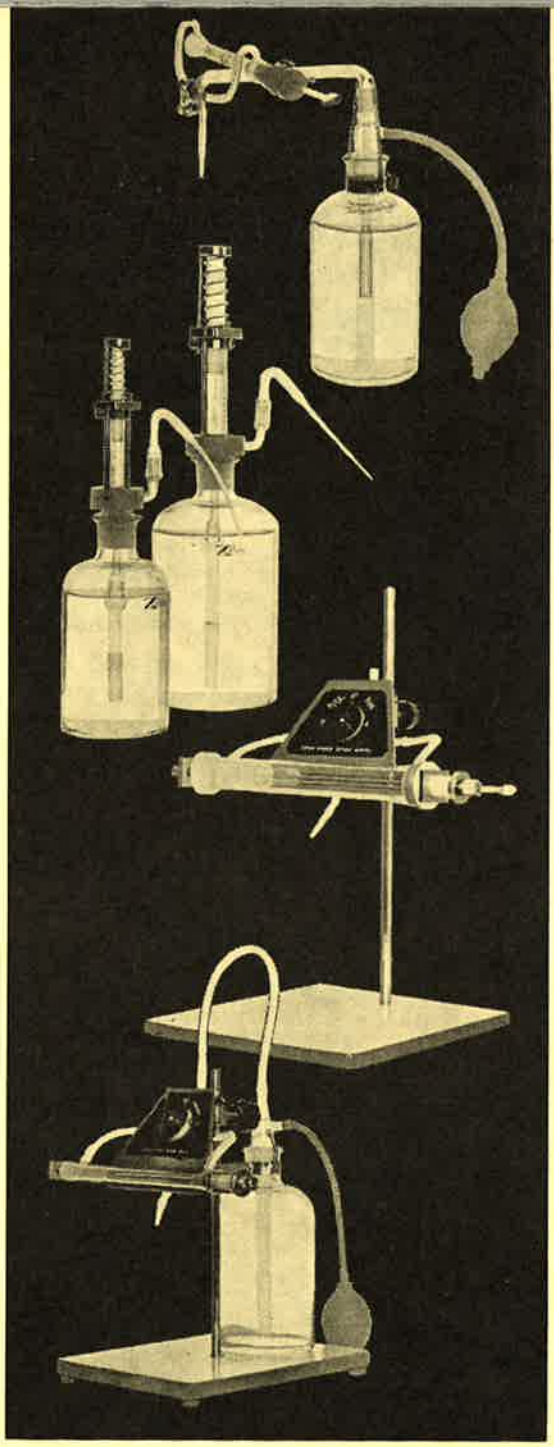
laboratorio-tarvikkeet hankitte meiltä edullisesti



Laboratoriotarvikevarastomme on todella laaja. Tarvikkeidemme korkea laatu, hintojen edullisuus ja runsas valikoima takaavat Teille nopeat ja taloudelliset hankinnat.

Varastossamme olevista tavararyhmistä voimme mainita:

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