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Sample Contamination with NMP-oxidation Products and Byproduct-free NMP Removal from Sample Solutions

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1-Methyl-2-pyrrolidinone (NMP) is widely used as a solvent for coal-derived products and as eluent in size exclusion chromatography. It was observed that sample contamination may take place, through reactions of NMP, during extraction under refluxing conditions and during the process of NMP evaporation to concentrate or isolate samples. In this work, product distributions from experiments carried out in contact with air and under a blanket of oxygen-free nitrogen have been compared. Gas chromatography/mass spectrometry (GC-MS) clearly shows that oxidation products form when NMP is heated in the presence of air. Upon further heating, these oxidation products appear to polymerize, forming material with large molecular masses. Potentially severe levels of interference have been encountered in the size exclusion chromatography (SEC) of actual samples. Laser desorption mass spectrometry and SEC agree in showing an upper mass limit of nearly 7000 u for a residue left after distilling "pure" NMP in contact with air. Furthermore, experiments have shown that these effects could be completely avoided by a strict exclusion of air during the refluxing and evaporation of NMP to dryness.

Introduction

1-Methyl-2-pyrrolidinone (NMP) is a powerful solvent for extracting coal and coal-derived materials. It has, in past work, been used as a pure solvent, and in solution with carbon disulfide, tetracyanoethylene, and other solvents.[1-14]

NMP has also proved useful as an eluent in size exclusion chromatography (SEC).[15-18] The technique relies on separating analytes in solution on the basis of their molecular sizes, as expressed by their hydrodynamic volumes in solution. The method relates elution time data of samples to their molecular masses (MMs) through a calibration curve. In turn, the calibration curve is obtained by plotting logarithms of known MMs of standard materials (log MM) against their elution times. Pure NMP is known to be a good solvent and eluent for nearly all coal-derived "liquids" studied. During SEC in NMP, elution times of a wide range of materials, including polymeric samples such as polymethylmethacrylates were observed to be less dependent on chemical structure than elution times in other classical eluents, such as tetrahydrofuran or pure chloroform.[16,19-21] More recently, 6:1 v/v solutions of NMP and chloroform have been shown to further reduce the effect of molecular structure on elution time during SEC.[22]

When pure NMP is used as eluent, bimodal chromatograms are usually obtained from most coal-derived samples, such as tars and pitches. Lighter distillate fractions may give single peaks.[18] As explained elsewhere,[19,21] the early eluting peaks tend to indicate the presence of material with very large (e.g., >100 000 u) apparent MMs. More detailed study of these apparently very large mass fractions would be aided by isolation from the whole sample, and SEC allows collecting successively eluting sample fractions in isolation. However, removing the NMP solvent from recovered elution fractions has proved problematic. Work done in our laboratory has suggested that samples may be contaminated with NMP-derived products,

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during attempts to remove the solvent by evaporation, to isolate the analyte. The complication was first confirmed through sample coloration, during attempts to dry-off aliquots of "pure" NMP.

Although NMP is widely used (cf., e.g., White et al.[13]), no clear consensus view appears to have been established on the effect of atmospheric oxygen on its behavior. There are reports in the literature showing NMP extractions carried out under a nitrogen blanket.[3,23] Others do not appear to have deliberately excluded ambient air during extraction or solvent removal.[24,25] A more recent study[26] confirmed that NMP undergoes polymerization during coal extraction at higher temperatures (350–450 °C), possibly due to the presence of oxygen from either the sample or from ambient air. The study showed the presence of some compounds that are likely to be oxidation products of NMP, such as N-methyl succinimide. Working with probe MS, an ion of m/z 129 was observed, suggesting oxidation products of NMP by addition of two oxygen atoms, as well as dimers (m/z 256), trimers (m/z 368, having lost an oxygen), and more highly polymerized material from the ion m/z 129.

The structures of the larger mass compounds observed during these analyses remained unknown. However, the observation of signals from fragment ions during these analyses strongly suggested that the material analyzed predominantly originated from the solvent rather than from the coal extract. This is because coal-derived material would be expected to show relatively intense molecular ions with only minor fragment ions, and it is clear that the spectra shown indicate the reverse.

Meanwhile, there have been suggestions that NMP is reactive in the presence of coal and coal-derived materials and is responsible for breaking carbon oxygen bonds when used at its boiling point, even under nitrogen.[27] In other work, there have been reports indicating that NMP is chemically inert during extraction and does not polymerize or react with coal or coal-derived materials, when operations are carried out under a nitrogen atmosphere.[23,28] These discrepancies could be related with the sensitivity of the analytical techniques and the ability to detect changes in NMP.

The SEC procedure used in our laboratory has involved purging air from the eluent (NMP) reservoir, by passing helium through the reservoir before turning on the solvent pump. Samples prepared for injection were made up in NMP solution at room temperature, with no deliberate effort to exclude ambient air. The small volumes of solution injected (20 μL) did not appear to cause spurious peaks in the chromatograms of sample solutions prepared at room temperature.

This sample preparation sequence has been checked in several ways. Injection of NMP alone after exposure to air did not give any signal. Actual sample fractions recovered as effluent from the column have been reinjected without concentrating. These samples showed no significant change in elution time, compared to their initial elution times. There was no indication of extra peak formation due to possible reactions of NMP at ambient temperature or during operation of the column at 80 °C.[17]

However, when fractions of samples collected from preparative scale SEC in NMP solvent were dried to remove NMP under vacuum, pyrolysis-GC-MS clearly showed signals corresponding to both residual NMP and to NMP dimers.[29] In this particular case, the SEC fraction selected corresponded to solvent in the valley between the two peaks of the tar sample chromatogram. To investigate the possibility of reactions of NMP with itself, a number of blank tests were performed. Pure NMP was evaporated under vacuum ($\sim 10^{-3}$ mbar) at different temperatures. At temperatures above 100 °C the NMP quickly turns yellow, then brown, leaving a dark-colored residue on evaporation. At lower temperatures the coloring was less intense, leaving behind a pale yellow residue when all solvent was evaporated.

These residues were redissolved in NMP and examined by SEC; the chromatograms showed bimodal distributions similar to those observed for coal tars and pitches. Similar residues were observed when pure NMP was distilled using a micro-distillation system, even when the system was purged with oxygen-free nitrogen for 10 min before heating. It could thus be observed that NMP-induced contamination during solvent evaporation (to recover solute) is possible. Furthermore, SEC chromatograms of the residues clearly showed that possible contamination by NMP-derived substances was likely to lead to the formation of material that could interfere with the characterization of actual coal-derived samples.

In other work[30–33] several coal tar fractions were dried for examination by solid state ^{13}C NMR. The fraction recovered from solution in NMP showed signal at around 140 ppm, where carbonyl functionalities are normally observed (similar to those observed for humic acids), as well as an increased aliphatic carbon content. However, during the examination of quaternary aromatic carbon in a coal extract and its hydrocracked products,[34] NMP had not been used to fractionate the sample and no significant presence of carbonyl carbon had been detected. Taken together, these findings strongly suggested that the carbonyl and aliphatic functionalities reflected the presence of residual NMP in the solid samples, either as unevaporated NMP or as polymeric byproduct.

This paper presents work done to study, in isolation, the conditions under which NMP oxidation and/or polymerization might occur. The aim was to arrive at robust methods for removing NMP from sample solutions without contaminating the original sample. Pure NMP blanks and solutions with other solvents were evaporated, and the residues were tested for contaminant formation. The techniques used for these tests included SEC, UV-fluorescence spectroscopy, LD-MS, gas chromatography (GC), and GC-mass spectrometry (GC-MS).

Experimental Section

Two sets of experiments were carried out in order to study the extent of NMP oxidation. In the first series of experiments, blanks

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of 6:1 NMP/CHCl₃ (volume ratio) mixtures and several samples dissolved in this mixture were dried under a nitrogen blanket and in ambient air. The concentration of the prepared solutions was on the order of 0.1 mg mL^{-1}. In all cases, the amount of liquid dried was 3.5 mL. Heat guns (DeWALT DW 340K) were used in the drying process; a heat gun was located at the bottom of the vial when drying under air, and an additional heat gun was located at right angles to the top of the vial when drying under N₂. The heat guns were configured to keep the maximum temperature during the drying at about 60 °C. Additionally, a flow of N₂ gas was introduced above the liquid during these latter drying tests. After drying, the samples were redissolved using the same volume of NMP/CHCl₃ 6:1 mixture and analyzed by SEC.

In the second set of experiments, 300 mL of NMP were refluxed for a period of time equivalent to those of actual sample extractions, either under a N₂ blanket or in ambient air. In the former case, N₂ was bubbled into the NMP for 30 min before starting the reflux. In the reflux experiments, samples of about 2 mL were taken from the "extraction flask" at different time intervals (up to 8 h). Finally, the liquid remaining in the flask was distilled, under the same atmosphere (N₂ or air) of the previous blank extractions. Samples of the distillate and residue were taken at different times during the distillation. Additionally, the presence of a solid residue in the distillation flask was observed. Such solid residues were dissolved in NMP and characterized by SEC alongside the other samples.

Both, drying and reflux tests, as well as SEC analysis, were carried out in duplicate to check the repeatability of the experiments.

SEC runs were carried out in a 30 cm long, 7.5 mm o.d. column, packed with 5 μm polystyrene-divinylbenzene polymer particles (Mixed-D column, Polymer Laboratories Ltd., UK) that was operated at 80 °C, at an eluent flow rate of 0.50 mL min^{-1}. The solvent was either a mixed solution of NMP and CHCl₃ (volume ratio 6:1) or pure NMP. Detection was by using a Perkin-Elmer LC290 variable wavelength UV-absorbance detector at 300 nm. Samples were dissolved in NMP/CHCl₃ (volume ratio 6:1), with about 0.2 mg mL^{-1} concentration. The calibrations and operating conditions have been previously described in detail.[22,35]

GC analysis was carried out on a Hewlett-Packard 5890 chromatograph with a flame ionization detector and an OV 1701 capillary column (25 mm × 0.22 mm i.d.). Hydrogen was used as a carrier gas at a flow rate of 2 mL min^{-1} and a splitting ratio of 1:87. The oven temperature was programmed to rise at a rate of 4 °C min^{-1}, from 50 to 260 °C, with this temperature being maintained for 10 min. The injector and detector temperatures were 300 °C.

GC-MS was performed with a Finnigan MAT CGQ ion trap mass spectrometer, with electron ionization (EI), employing the same capillary column and temperature program as used in the GC analysis. The ion source and transfer line temperatures were 230 and 250 °C, respectively. Data were acquired in full scan mode between *m/z* 50–550; a solvent delay of 6 min was used. The most probable compounds were identified by comparing their mass spectra to the mass spectra contained in the NIST library in the MS database and from their retention times, standard compounds being used when available.

MALDI-MS. A Bruker Daltonics Reflex IV MALDI-TOF mass spectrometer was used for LD-MS. Because the kind of samples examined were able to absorb the UV-laser wavelength of 337 nm, no matrix was used, and only positively charged ions were analyzed. The digital gains (DG) were set to their lowest level (1×).Ten spectra were summed using the pulsed ion extraction (PIE) method on the same sample spot. Reflector TOF mode was used with no extraction delay within the ion mass range up to *m/z* 6000.

Materials. All the solvents were HPLC grade and were used as received: NMP (peptide synthesis grade; Rathburn Chemicals, UK) and CHCl₃ (HPLC grade, BDH, Poole, UK). Petroleum-derived samples analyzed were an asphaltene fraction from a crude oil "B" prepared by the standard method ASTM D 3279–97, and samples
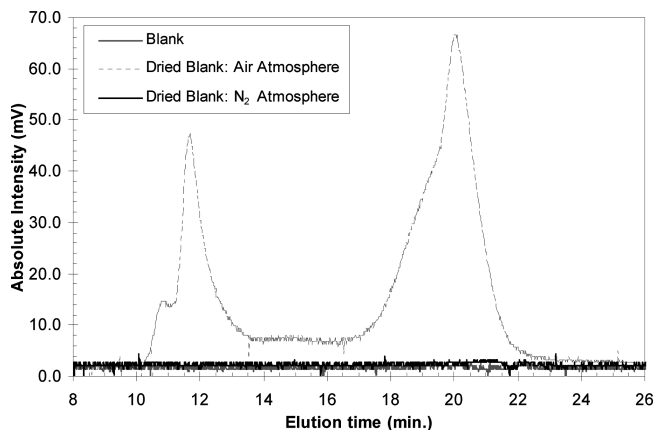
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Figure 1. SEC on the "Mixed-D" column of blank of NMP/CHCl₃ (6:1) samples dried under N₂ and air atmospheres. NMP/CHCl₃ (6:1) as eluent and detection at 300 nm by UV absorbance.

of deposits obtained after subjecting the crude oil "B" to high temperature (390 °C) under nitrogen at high pressure (80 bar) for 6.5 h. A brief description of the properties of the crude B and its fractions is shown in a previous work.[22] The nitrogen gas was OFN grade.

Results And Discussion

Drying Test Results. As already explained, the first series of experiments involved drying blanks of 6:1 mixtures of NMP/CHCl₃ and solutions of several samples dissolved in the same mixture (0.1 mg mL^{-1}). Experiments were performed under a N₂ blanket and in ambient air, following the method described in the experimental section. After evaporation to dryness, the residues were redissolved using the same volume of NMP/CHCl₃ (6:1 v/v) mixture and characterized by SEC.

Figure 1 presents the SEC chromatogram of a blank sample of 6:1 NMP/CHCl₃ and of two aliquots of the same solvent that were dried under air and under a N₂ blanket and redissolved in fresh solvent. The results show no evidence of extraneous peaks from either the fresh NMP/CHCl₃ mixture or the sample dried under a N₂ blanket, always keeping the maximum temperature of drying below 60 °C. However, the chromatogram from the sample dried in ambient air gave a bimodal distribution, with an excluded peak between 10 and 13 min, and a retained peak from 17 to 22 min. The calibration of the column[22] indicates that a 17 min retention time corresponds to a polystyrene mass of about 3500 u.

It has been suggested that the excluded material is an artifact due to aggregation of smaller molecules. At the levels of dilution prevalent in SEC systems (<0.001 mg mL^{-1}), the excluded peak is unlikely to result from aggregates of smaller molecules.[16,17,22] An alternative explanation for the presence of the excluded peak would suggest that it represents changes in conformation or structure rather than an increase in mass, that is, changing from flexible to rigid three-dimensional structures, although this is an issue that remains to be resolved.

In Figure 1, the excluded peak was smaller than the retained peak, it was noted that the intensity of the excluded peak was relatively high (almost 45 intensity units for the excluded peak vs 65 for the retained peak). Thus, the conditions of drying of the NMP/CHCl₃ samples under ambient air lead to contamination and spurious signal, giving unreliable data with artifact peaks in both the retained and excluded regions of the SEC chromatogram.

In these runs, the volume of solvent (NMP/CHCl₃ 6:1 mixture) added to redissolve the samples was the same as the
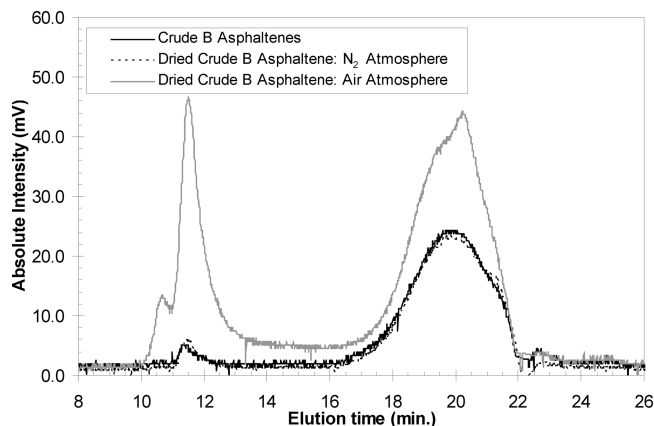
Figure 2. Crude B asphaltenes: initial and dried solutions (NMP/CHCl₃ 6:1) under air atmosphere; SEC chromatograms on Mixed-D, using NMP/CHCl₃ 6:1 as eluent, and detection at 300 nm UV absorbance.
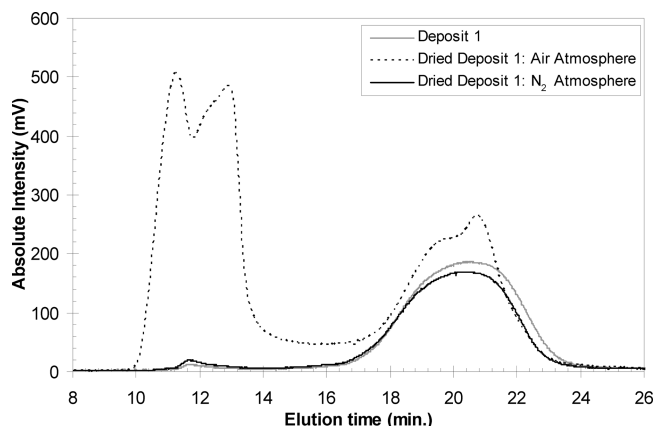

Figure 3. Deposit 1 from Crude B: initial and dried solutions (NMP/CHCl₃ 6:1) under N₂ and air atmospheres; SEC chromatograms on Mixed-D, using NMP/CHCl₃ 6:1 as eluent, and detection at 300 nm UV absorbance.
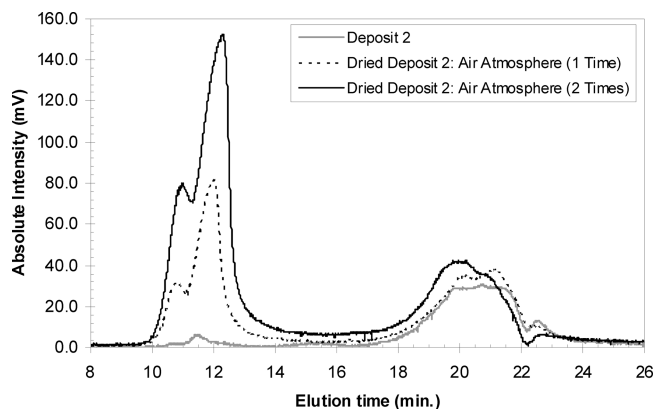

Figure 4. Deposit 2 from Crude B: initial and dried solutions (NMP/CHCl₃ 6:1) under air atmosphere; SEC chromatograms on Mixed-D, using NMP/CHCl₃ 6:1 as eluent, and detection at 300 nm UV absorbance.

volume of the original sample before drying. This procedure allows signal intensity to be solely dependent on the concentration of the solute. Figures 1−4 are therefore presented without area or peak normalization; in each case the volume of sample injected was kept constant at 20 μL.

Figures 2−4 show the effect of drying the mixed NMP/CHCl₃ solvent from solution of petroleum-derived deposits and asphaltenes (in NMP/CHCl₃) under several conditions. It must be noticed that the deposit samples correspond to the solid residues obtained after subjecting the crude oil B to high

temperature (390 °C) under nitrogen at high pressure (80 bar) for 6.5 h. In all cases, complete drying of the solvent mixture under ambient air appears to have led to massive excluded peaks between 10 and 14 min and smaller changes in the retained peak. Moreover, the excluded peak intensity increased with the number of times that the sample was dried and redissolved (Figure 4). The polystyrene calibration masses corresponding to the early lift-off of the retained peaks are about 3500 u (Figures 2 and 4) and 7600 u (Figure 3).

To summarize, all chromatograms obtained after drying the samples under ambient air were found to contain unresolved excluded peaks with two maxima, centered around 11 and 12 min, respectively. The relative intensities of these peaks depended on the sample. Whereas both maxima were similar in height for the "Deposit 1" sample (Figure 3), for Crude B asphaltenes (Figure 2) and "Deposit 2" (Figure 4) the second peaks were five and two times higher, respectively. Furthermore, in all the cases, the excluded peak was higher than the retained peak after drying the samples under ambient air, whereas it had been much smaller in the original samples. This is more clearly apparent in the "Deposits" samples, (Figures 3 and 4) where the intensity of the excluded peak is twice as high as the retained peak intensity. Rather than being a cumulative effect, these data suggest the occurrence of synergistic effects between the excluded material in the sample and the NMP-derived material apparently produced during the drying process.

Similar results were obtained from identical tests performed with pure NMP and NMP/sample solutions prepared using coal-derived materials (not shown). In these experiments, the use of a N₂ blanket did not completely mitigate the formation of reaction products, although it did greatly reduce them. To avoid the formation of NMP reaction products it was found necessary to degas the NMP solutions under vacuum (10⁻³ mbar), followed by a nitrogen purge (repeated at least 3 times) before drying under a nitrogen blanket at low temperature (∼80 °C).

Refluxing and Distillation Results. The next test to evaluate the reactions of NMP under oxidizing conditions consisted of several blank extractions using "pure" NMP as solvent, under N₂ and ambient air. In the case of the N₂ atmosphere test, oxygen was purged from the system by bubbling N₂ for 30 min through the sample solution before heating. During tests under ambient air, the system was open and air was not purged from either the solvent or the reflux system before heating.

During the refluxing process, samples were collected at different times and characterized by SEC using NMP as eluent. In the course of the blank "extractions," refluxing pure NMP in the presence of air, a rapid darkening of the solvent was observed. This was the first visual evidence of NMP degradation under these conditions. This observation would not have been possible in the presence of a coal- or petroleum-derived sample in solution.

The results for refluxing under ambient air are shown in Figure 5. All the chromatograms show that the major part of the sample eluted between 18 and 23 min, with a smaller peak between about 10−11 min. The main peak at 18−23 min, which corresponds to the lower MM components, shows an increase in intensity with reflux time. A double SEC peak was observed in the signals of the retained peak for reflux times of 3 h and longer, with maxima at 20.1 and 20.6 min.

The polystyrene calibration for this column indicates that for the retained peaks, the lift-off from baseline around 18 min corresponds to a polystyrene mass of about 1500 u. The maxima at 20.1 and 20.6 min corresponded to 470 and 370 u respectively, while the low-mass end of the peaks corresponded to
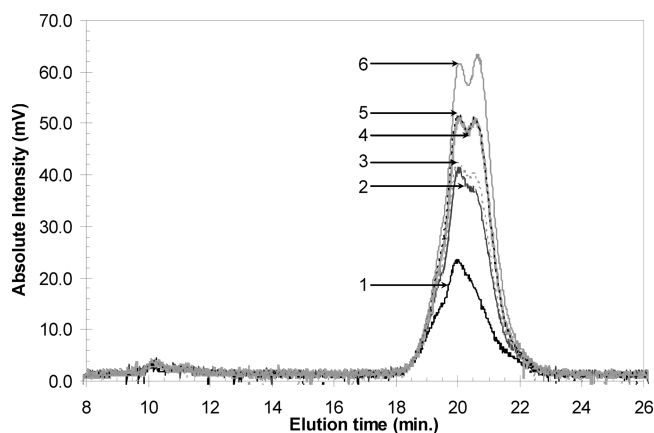
Figure 5. Evolution of NMP refluxed under air atmosphere with time analyzed by SEC (Mixed-D, using NMP as eluent, and detection at 300 nm UV absorbance). Curves are equivalent to reflux times of 1: 1, 2: 2, 3: 3, 4: 4.30, 5: 5:30, and 6: 8 h.
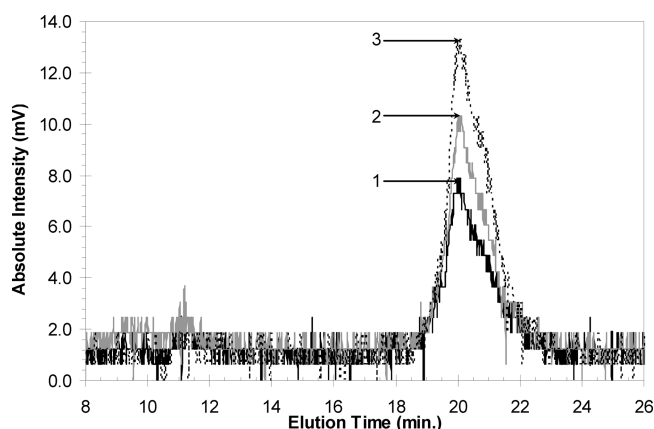

Figure 6. Evolution of NMP refluxed under N_2 atmosphere with time analyzed by SEC (Mixed-D, using NMP as eluent, and detection at 300 nm UV absorbance). Curves are equivalent to reflux times of 1: 1, 2: 3, and 3: 5 h.
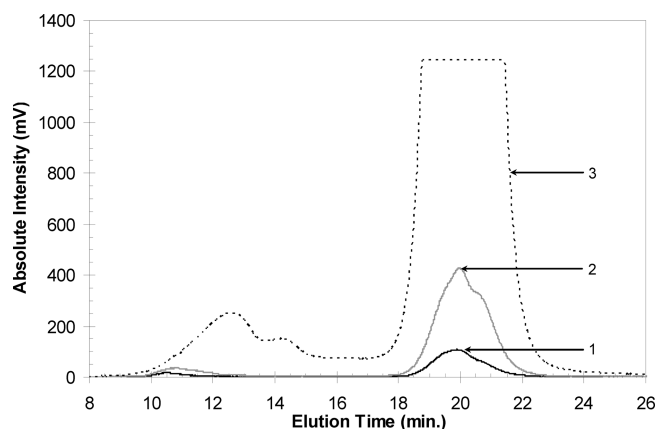

Figure 7. Residues of distillation of NMP refluxed under air atmosphere at different volumes of distilled analyzed by SEC (Mixed-D, using NMP as eluent, and detection at 300 nm UV absorbance). Curves are equivalent to percentage of volume distilled of 1: 16; 2: 50, and 3: 83%.
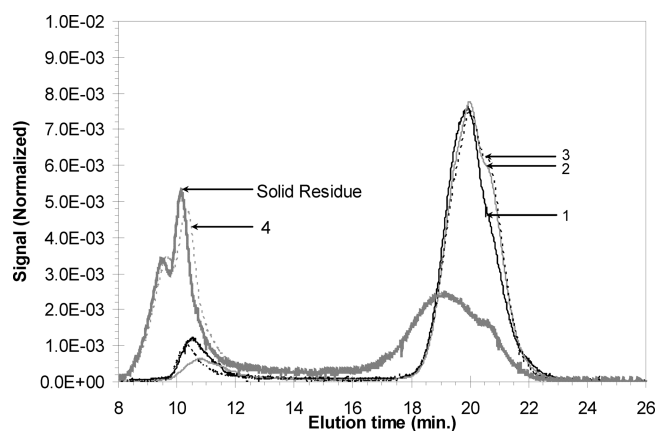

Figure 8. Residues of distillation of NMP refluxed under ambient air at different levels of distillation, characterized by SEC (Mixed-D, using NMP as eluent; detection at 300 nm UV absorbance). Curves are equivalent to percentage of volume distilled of 1: 16, 2: 50, 3: 83, 4: 99%, and solid residue.

about 120 u. The mass values at the longer elution times were not taken from the polymer calibration; they were estimated from the elution times of different PAH and other small molecules.[22]

In Figure 5, the peaks that appeared near 10−11 min corresponded to early eluting, apparently large sized material excluded from the column porosity. The intensity of these excluded peaks was significantly smaller than the intensity of signal showing under resolved peaks and remained fairly constant during the 8 h of the reflux test. As signaled above, the excluded peak appears to be related to the presence of three-dimensional structures.[22] The observed results suggest little or no build up of apparently large molecular mass material or three-dimensional molecules.

Results from reflux under a N_2 blanket are presented in Figure 6. All chromatograms showed a main peak around 19−23 min, the intensity of which increased with the reflux time. Smaller peaks, similar in size, were detected in the excluded region (around 11 min). These changes suggest that not all oxygen could be removed from the system before starting the reflux. It is important to note, however, that peak intensities were far lower than those shown in Figure 5 when the reflux was performed under ambient air.

The result underlines the importance of avoiding the presence of oxygen in proximity with the samples. It appears that the degassing of NMP solutions and drying under vacuum (10^{-3} mbar) described above (and not thought of as essential for the drying of small-volume samples), should really be considered as strictly necessary under evaporation to dryness and refluxing, involving relatively large volumes of solvent, or in samples to be characterized by more sensitive analytical techniques such as ^{13}C NMR (e.g., Begon et al.[34]).

Taken together, these results show a remarkable increase in signal under the excluded peak, when evaporating to dryness under ambient air (Figures 1−4). Products from the refluxing of samples under air showed the formation of less artifact material (Figure 5). To check the conditions that promote this effect, a distillation of the liquid sample obtained by reflux under ambient air was performed.

Distillation. Figures 7 and 8 show the SEC chromatograms of the distillation residues of NMP refluxed under ambient air, when (1) 16, (2) 50, (3) 83, and (4) 99% of the initial sample had been distilled off. At the end of the distillation process, a solid residue was recovered from the distillation flask. This residue was dissolved in NMP and also characterized by SEC.

The intensification of the signal from the samples in a progression from curve 1 to 3 in Figure 7 suggests an increase in concentration of NMP degradation products. In all cases, the injection volume was kept constant (20 μL) and the samples were injected as collected, without additional dilution. However, from curve 3 (83% distilled) onward, the signal obtained was too intense and saturated the detector, so the sample was diluted.
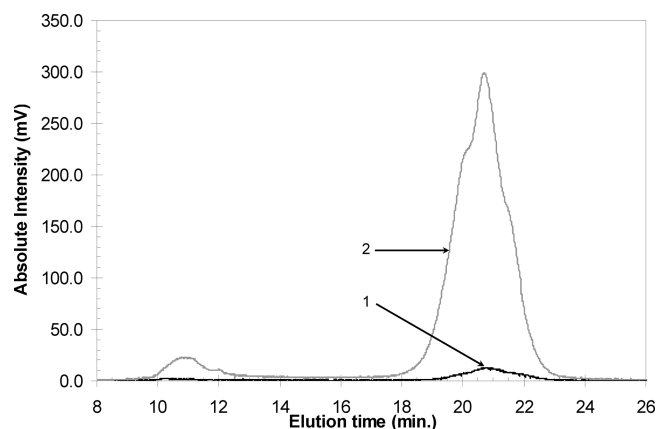
Figure 9. Distilled fractions from NMP refluxed under air atmosphere at different volumes of distilled analyzed by SEC (Mixed-D, using NMP as eluent, and detection at 300 nm UV absorbance). Curves are equivalent to 1: first distilled fraction, 2: last distilled fraction.

The comparison of all the samples and the solid residue is presented in Figure 8. In this Figure, the chromatograms were area normalized to facilitate the comparison.

The results show similar levels of signal for curves 1, 2, and 3, strongly suggesting that the concentration of the products increases during the initial steps of the distillation (Figure 7); however, there appears to have been no significant changes in the level of polymerization products. The intensity of the retained peaks were observed to increase, as the concentration of the smaller oxygenated compounds increases in the distillation flask (confirmed by GC-MS), up to 83% distillation of the sample solution (sample c). The results obtained for sample d and the solid residue showed the largest excluded peaks (between 8 and 12 min) with a double maximum at 9.5 and 10.2 min, approximately. The polystyrene calibration mass corresponding to the upper mass limit of the retained peak is 7600 u and is similar to the upper mass found for the deposit samples dried in air. These findings show that under drying conditions (high concentration of oxidized compounds) and in presence of air, NMP, or the oxidation products of NMP, polymerize into compounds of large apparent molecular size, or strictly, of large hydrodynamic volume.

Finally, the characterization of material that had distilled over (Figure 9) did not show the massive presence of these large polymeric compounds detected in the residues. However, the concentration of oxidized compounds in the first distilled fraction was lower than in the last fraction. Thus, it appears that smaller molecular mass oxidation products could either distill over or form polymerization products that would remain behind with the residue.

Several other studies have also reported observing the oxidation of NMP under various experimental conditions: oxidation in aqueous phase,[36,37] catalytic oxidation,[36,38,39] ozone oxidation,[40] and uncatalyzed reaction with air at different temperatures.[13,38] These studies have all reported the formation of some of the main, smaller molecular mass oxidation products: succinimide, N-methylsuccinimide (NMS), formylpyrrolidone (FP), N-hydroxymethylpyrrolidone (NHMP), 5-hydroxy-N-
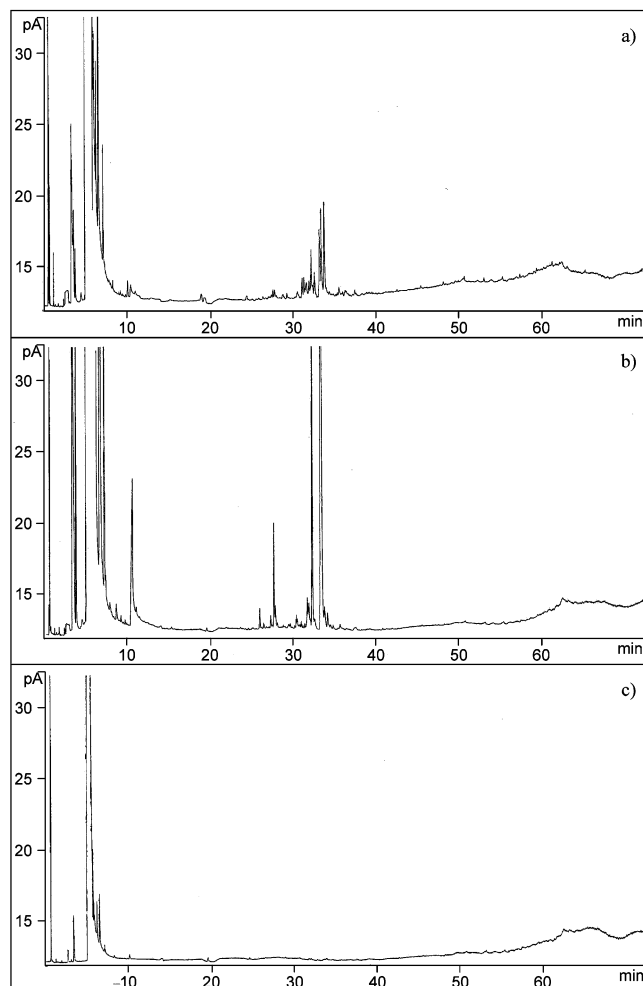

Figure 10. GC-FID chromatograms of: (a) final distilled fractions from NMP refluxed under air atmosphere, (b) NMP refluxed under air atmosphere for 8 h, and (c) sample of pure NMP.

methylpyrrolidone (5-HNMP), 2-pyrrolidone (2P), methylamine, formamide, acetamide, N-methylformamide, N-ethylacetamide, and dimethylacetamide.[37] Three main oxidation pathways ("A", "B" and "C") have been suggested by Poulain et al.[37]

Pathway A is based on the oxidation of NMP by substitution of carbonyl or hydroxyl groups at the α-carbon position. It is well-known that the α-carbon of lactams such as NMP and 2-pyrrolidinone is susceptible to H-atom abstraction.[38,39,41] This leads to the formation of an alkyl radical that reacts with dissolved oxygen to form a peroxy radical. This radical may subsequently decompose into NMS (N-methylsuccinimide) and 5-HNMP (5-hydroxy-N-methylpyrrolidone). The decomposition through a peroxide intermediate derived from O_2 substitution at the α-carbon seems to be the most probable pathway.[36]

Pathway B consists of the attack of OH radicals, which produces a hydrogen abstraction on the methyl group of NMP. This pathway takes place through the formation of another alkyl radical, which leads to the formation of FP (formylpyrrolidone) and NHMP (N-hydroxymethylpyrrolidone), through a peroxy radical. This second pathway has been previously mentioned by Friesen et al.[36] and Poulain et al.[37] in aqueous solution.

Pathway C is considered as less probable and more speculative than the previous two. An analogous pathway was mentioned by Horikoshi et al.,[42] who performed OH-oxidation of 2P (2-pyrrolidone) in the aqueous phase in the presence of

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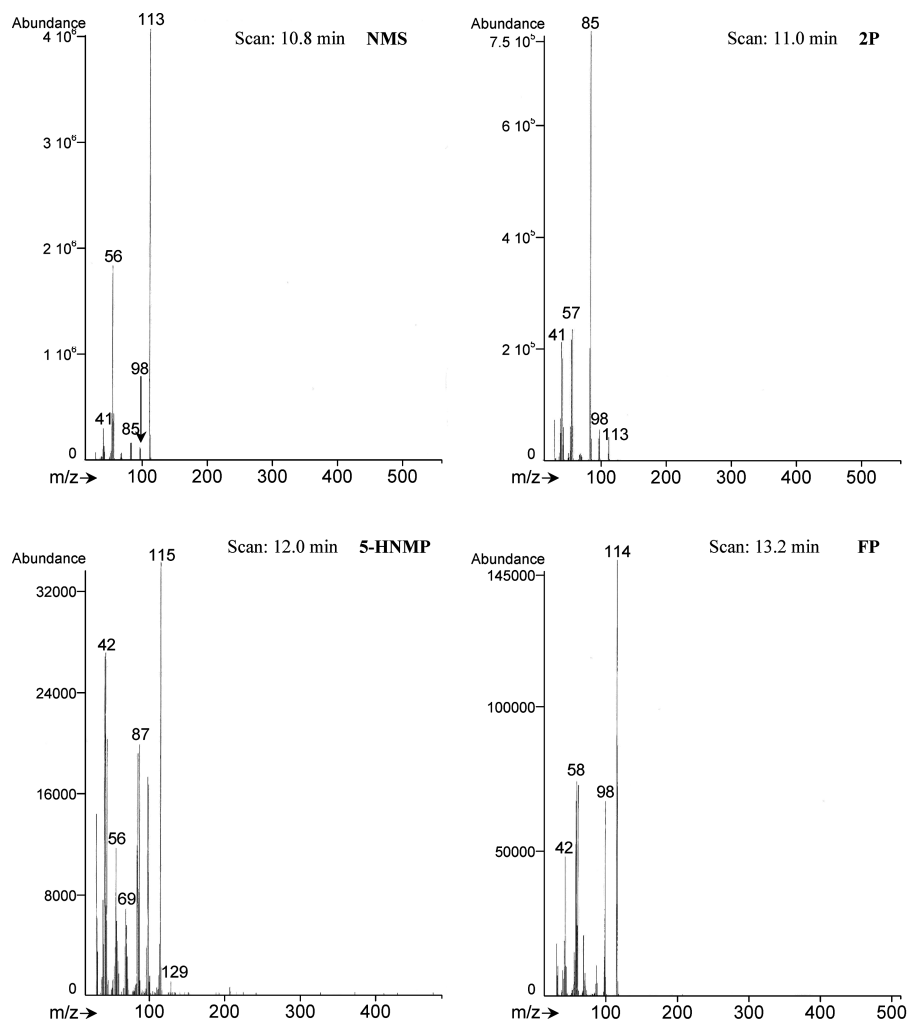(41) Masui, M.; Hara, S.; Ozaki, S. *Chem.Pharm. Bull.* **1986**, *34*, 975–979.

Figure 11. Mass spectra of products derived from the oxidation of NMP with retention times in the region 6−10 min.

solid phase TiO_2.[37] The pathway proceeds via a ring-opening mechanism, leading to the formation of N-methyl-4-aminobutanoic acid.

In addition to these initial oxidation pathways, other studies[26,29] show the presence of oxidation products when NMP is subjected to high temperatures or drying conditions in the presence of air. The detected products correspond to ion m/z 129, which may be an oxidation product of NMP derived by addition of two oxygen atoms (one as a second carbonyl group and one by oxidation of the methyl to methoxyl), as well as the dimer, trimer, and more highly polymerized materials of this compound. The SEC results showed in the current work suggest the presence of initial oxidation products as well as increasing amounts of polymerized material, depending on the intensity of the drying or distillation conditions. In order to identify as many reaction products as possible and to detect the presence of high molecular mass compounds, GC and LD-MS analyses have been performed on some of the distillation subfractions.

Three different samples were analyzed by GC: "GC-reflux", sample of NMP refluxed under ambient air for 8 h (Curve 6 in Figure 5); "GC-distilled", that is the final distilled fraction from NMP refluxed in the presence of ambient air (Curve 2 in Figure 9); and "GC-NMP", a sample of pure, that is, as received, NMP. Figure 10 shows the GC-FID chromatograms of these three samples. The chromatograms confirm the presence of compounds different from the original NMP, with a series of peaks before the

NMP signal (around 4 min) and two groups of peaks in the 6−10 and 28−35 min regions. Additionally, the chromatograms of GC-distilled (a) and GC-reflux (b) show a similar chromatogram, with groups of peaks that appear at similar retention times, although the concentration is higher for the GC-reflux sample (b).

These samples were also analyzed by GC-MS. The results showed the presence of N-methylsuccinimide (NMS) and 5-hydroxy-N-methylpyrrolidone (5-HNMP), products of pathway A; and 1-formyl-2-pyrrolidone (FP) or 2-Pyrrolidone (2P), from pathways B and C, respectively, in GC-reflux and GC-distilled samples in the groups of peaks around 6−10 min (Figure 11). On the other hand the scans obtained from the peaks in the 28−35 min region (Figure 12) show maximum signals at m/z 98, which could be related to the presence of different oligomers of NMP. In some of the scans the second peak in intensity was obtained at m/z 196 and was probably a dimer of NMP.

The products obtained during the reflux and distillation of NMP in the presence of ambient air are similar to those suggested by Poulain et al.,[37] apparently forming through pathways A and B cited above (NMS or FP), although these pathways do not explain the potential and progressive polymerization of the oxidized products. One feasible explanation is that oxygen from the oxidation products could act as catalyst in cross-linking reactions or establish C−C bonds, which leads to progressive polimerization.[43,44]

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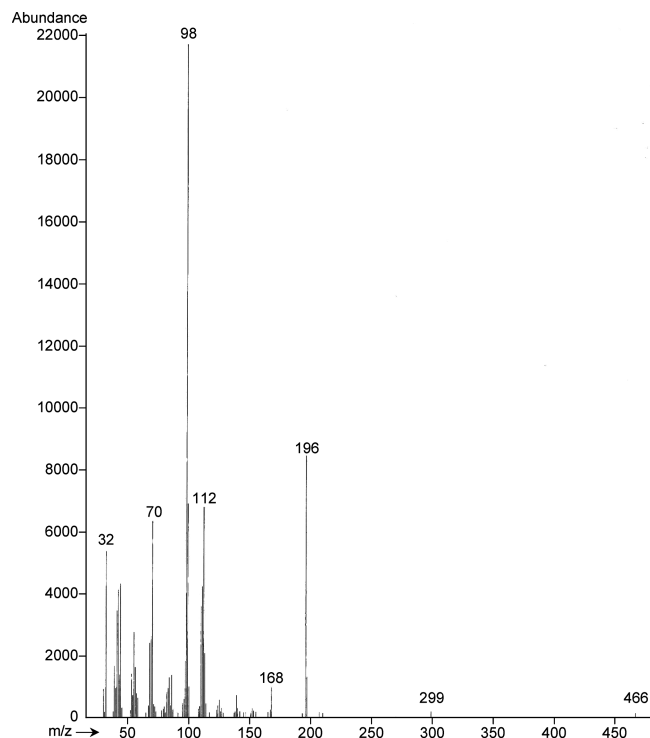
Figure 12. Mass spectrum of products derived from the oxidation of NMP with retention times in the region 28−35 min.
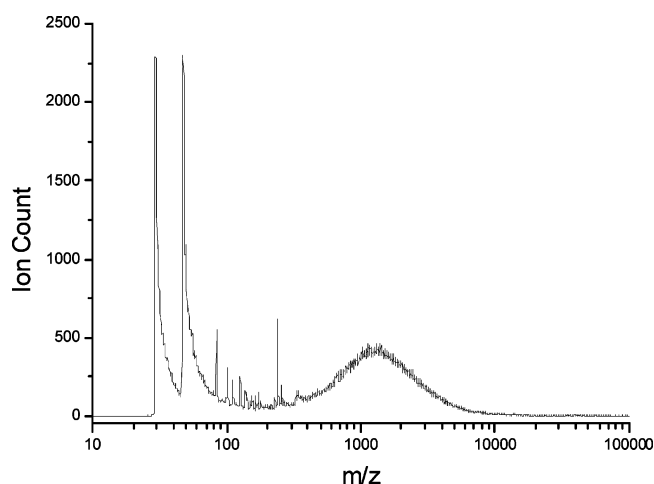

Figure 13. LD-MS spectrum of NMP reaction products from the residue recovered after vacuum drying (10^{-3} mbar, 95 °C) 10 mL of pure NMP. The spectrum was acquired with no delayed ion extraction time, with a laser power of 40% of maximum and 10 kV high mass accelerator voltage. The sample was applied neat to the metal surface of the target without the addition of a matrix.

Due to their low volatility, the heavier oligomers of NMP, identified previously by SEC, could not be detected by GC. Instead, presence of high molecular mass compounds in the solid residue was confirmed by LD-MS. The method used has been developed to improve the estimates of mass ranges for complex hydrocarbon mixtures and to avoid the generation of artifacts.[45] Figure 13 shows the LD-MS spectra of the solid residue obtained after the distillation (air atmosphere) in the ion extraction mode with no time delay before extraction, with a laser power of 40%

of maximum and 10 kV high mass accelerator voltage. These conditions were chosen because they most clearly illustrate the highest mass regions of the sample. The spectrum shows two different zones, a group of small peaks from *m/z* 70 to 200, and a second peak with a maximum intensity at about *m/z* 1500 and a mass range (*m/z*) from 400 to 6000. Such high mass polymerization products of NMP have not previously been reported. The mass spectral results are in good agreement with the estimates of the upper mass of the retained peaks of the SEC chromatograms as about 7000 g/mol in Figures 3 and 8. The mass ranges of the excluded peak of the SEC chromatograms have not been defined. These molecules may be of different conformation to the later eluting materials, and possibly not of significantly different mass.

Summary And Conclusions

Reactions of NMP taking place during extraction under refluxing conditions and during the process of NMP evaporation to concentrate or isolate samples have been studied. Experiments were carried out with blank solutions consisting of pure (as received) NMP.

The formation of NMP oxidation products of comparable molecular mass to NMP has been observed by GC and GC-MS, when blank extraction experiments were performed under refluxing conditions, in the presence of air. In addition to small oxidized molecules such as methylsuccinimide or 1-formyl-2-pyrrolidone, which confirm the process of oxidation reported in the literature, the data also indicated the presence of oligomers of NMP as the heaviest compounds detected in the drying products. Larger mass material would not be able to pass through the GC column. This is where techniques such as size exclusion chromatography and laser desorption-MS come into their own.

The residue from these experiments was found to contain polymerization products of masses up to 7600 u, observed by size exclusion chromatography (SEC) and confirmed by LD-MS. The heavier materials are thought to form through the polymerization of primary NMP oxidation products.

When NMP was evaporated to dryness at atmospheric pressure, under conditions not excluding air, the presence of NMP oxidation products was identified by GC and GC-MS. Once again, high mass material was identified in the distillation residues by size exclusion chromatography (SEC). The amount of material showing signal under the excluded peak (high apparent masses) in SEC increased with the intensity and duration of drying.

The formation of oxidation products (of comparable masses to NMP) as well as the heavier material, apparently formed through the polymerization of NMP oxidation products, could be suppressed by nitrogen blanketing the samples during heating and by degassing the NMP before use, under vacuum and through careful N_2-purging.

The results obtained clearly show that it is necessary to avoid the presence of air in the process of evaporating solutions to dryness and in the extraction of samples under reflux, when NMP is used as solvent.

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