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EDGEWOOD
RESEARCH, DEVELOPMENT & ENGINEERING CENTER
U.S. ARMY CHEMICAL AND BIOLOGICAL DEFENSE COMMAND

ERDEC-CR-107
(MRI 3370-M)

PHYSICOCHEMICAL EVALUATIONS OF SELECTED SOLVENTS FOR USE IN DECONTAMINATING AGENT: MULTIPURPOSE (DAM) FORMULATION

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March 1994

20030226209

Aberdeen Proving Ground, MD 21010-5423

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (*Leave blank*)

2. REPORT DATE
1994 March

3. REPORT TYPE AND DATES COVERED
Final, 92 Feb - 93 Dec

4. TITLE AND SUBTITLE
Physicochemical Evaluations of Selected Solvents for Use in Decontaminating Agent: Multipurpose (DAM) Formulation

5. FUNDING NUMBERS
C-DAAL03-91-C-0034
TCN-93027
D.O.-0623

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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Kansas City, MO 64110

8. PERFORMING ORGANIZATION REPORT NUMBER
ERDEC-CR-107
(MRI 3370-M)

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
DIR, ERDEC,* ATTN: SCBRD-RTC, APG, MD 21010-5423

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
COTR: Philip Bartram, SCBRD-RTC, (410) 671-5660
*When this study was conducted, ERDEC was known as the U.S. Army Chemical
(Continued on page ii)

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)

A series of aprotic, polar solvents were evaluated as potential replacements for N-cyclohexyl-2-pyrrolidinone currently used in Decontaminating Agent, Multipurpose (DAM) formulations. Out of nearly 40 solvents examined, only sulfolane and 3-methylsulfolane exhibited all the required properties. These two solvents (40/60 vol/vol) in admixture with 11 vol% water provided a low viscosity fluid with a -25 °C melting point. On standing for 6 hr, the sulfolane-water-HTH formulation lost <6% of its oxidative strength. These two sulfolanes have very high boiling points and low (>0.1 Torr) vapor pressure at 25 °C. The available literature indicates that the sulfolanes have low toxicity. Sulfolane is a "near" solvent for the K-125 polymeric thickener, while 3-methylsulfolane is a "good" solvent. The K-125 polymer powder showed high swelling and agglomeration in an aqueous solution of 3-methylsulfolane (35 vol %). A very simple calorimeter was used to compare the rate of heat release (≅rate of reaction) for three sulfolane-based formulations against the pyrrolidinone formulation. The reaction rate of the DAM formulation containing the mixed sulfolane solvent system was at least 50% faster.

14. SUBJECT TERMS

Decontaminating agent muitipurpose
Sulfolane and 3-methylsulfolane
1-substituted-2-pyrrolidinones
Oxidative stability
High test hypochlorite
Solubility parameters

15. NUMBER OF PAGES
105

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

11. SUPPLEMENTARY NOTES (Continued)

Research, Development and Engineering Center, and the Contracting Officer's Technical Representative was assigned to the Physical Protection Directorate.

PREFACE

The work described in this report was authorized under Contract No. DAAL-03-91-C-0034, Task Control No. 93027, Delivery Order No. 0623. This work was started in February 1992 and completed in December 1993.

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Acknowledgments

Midwest Research Institute (MRI) wishes to acknowledge the guidance provided by the DAM Working Group and Philip Bartram of the U.S. Army Edgewood Research, Development and Engineering Center (ERDEC),* who served as program Technical Monitor.

The work at MRI was designated Project No. 3370-M and was performed under the supervision of Dr. Cecil C. Chappelow, Senior Advisor, who served as project leader. Personnel contributing to the project were Howard W. Christie, Research Associate; Thomas J. Byerley, Senior Chemist; and Gary R. Cooper, Staff Chemist. The administration of the project was provided by the Engineering and Environmental Technology Department of MRI, Dr. Charles F. Holt, Director.

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*When this study was conducted, ERDEC was known as the U.S. Army Chemical Research, Development and Engineering Center, and the Contracting Officer's Technical Representative was assigned to the Physical Protection Directorate.

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SECTION 1

INTRODUCTION

The U.S. Army Edgewood Research Development and Engineering Center (ERDEC) has a requirement for a research effort structured to investigate, identify, and test new solvents for polymer-thickened agent dissolution that meet the Decontaminating Agent: Multipurpose (DAM) formulation requirements. The DAM formulation is currently being developed as a substitute for DS2. The DAM formulation contains: high test hypochlorite (HTH) (calcium hypochlorite), *N*-cyclohexyl-2-pyrrolidinone (CHP), and water. Recent tests with the DAM formulation have identified several problem areas regarding CHP; hence, a replacement for the CHP constituent of the DAM formulation is sought.

The overall objective of this program was twofold:

- To identify new organic solvents to substitute for *N*-cyclohexyl-2-pyrrolidinone.
- To conduct laboratory tests to identify the physical and chemical properties of the new solvents as they relate to decontamination.

A number of requirements have been established for both the organic solvent and the DAM formulation. The basic requirements for the solvent system used in the DAM formulation are:

- The solvent must not react appreciably with high test hypochlorite (HTH).
- The solvent must dissolve thickened agent (i.e., TGD, THD).
- The solvent must not form a separated phase when mixed with water and HTH.

To meet overall property/performance requirements, the DAM formulation:

- Must not present any uncontrolled safety or health hazards at any point in the life cycle when reasonable care is exercised in handling and use.
- Must be nonflammable at any operational temperature (–32° to 49°C).
- Must be compatible with equipment, vehicles, and aircraft painted with chemical agent-resistent coating (CARC), and chemical protective clothing.
- Must be easily mixed both mechanically and manually and not require constant agitation.
- Must be capable of decontaminating the exterior of all nonabsorbing materials to a minimum acceptable value (MAV) of not less than 90% as effectively as DS2 with performance objective of 100% as effective as DS2. These levels of decontamination shall be against all probable threat chemical/biological agents including toxins.
- Will not leave any signature by visual, infrared, ultraviolet, thermal, or radar after rinse (if needed).
- Must have a mixed DAM temperature range of 0° to 49°C.
- Must be stable and effective if salt or brackish water is used for mixing or rinsing.
- Must have a packaged, covered shelf life of 2 to 5 years.
- Will have a pot life of at least 5 hr.
- Must be compatible (not interfere) with standard and developmental detector devices such as the Chemical Agent Monitor (CAM) and M8 and M9 Paper, Chemical Agent after rinsing.

The requirements related to evaluation of reactivity to active agents was not to be demonstrated in this program. Also, compatibility with chemical agent monitors was not to be demonstrated. A thickened agent simulant, 5 wt % K-125 polymer dissolved in diethylmalonate, was used in place of actual agents for demonstration purposes.

The research approach consisted of a series of sequential tasks, which are summarized as follows:

- Identify by literature search and market survey commercially available and environmentally safe organic solvents to substitute for CHP which has a high probability of meeting requirements for DAM.
- Select and/or synthesize the best candidate organic solvents that have the potential of meeting the requirement characteristics.
- Determine the best analytical procedures and test methods to study the new solvents selected or formulated to determine whether they can possibly meet the DAM formulation solvent requirements.
- Test the solvents selected or formulated against the DAM formulation solvent requirements using simulants only.
- Identify the best formulations using the results from the tests performed and provide 1 L of each of the best candidate solvents.

The remainder of this final report is organized as follows. Section 2 describes the experimental work. Section 3 presents the results and a discussion of the results. Section 4 provides a summary of the investigation and conclusions drawn from the research. References and four appendices are provided at the end of the report.

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SECTION 2

EXPERIMENTATION

The materials, test methods, laboratory procedures, and evaluation techniques employed during the course of this exploratory development program are described in this section.

2.1 CHEMICALS, REAGENTS, AND SOLVENTS

The sources of the chemicals, reagents, and solvents used in this research program are identified in this section.

2-Methyl-2-propanol (*tert*-butyl alcohol), 99%, Aldrich Chemical Company, Milwaukee, Wisconsin

2-Pyrrolidinone, 99%, Aldrich Chemical Company, Milwaukee, Wisconsin

1-Methyl-2-pyrrolidinone, practical grade, Eastman Kodak Company, Rochester, New York

1-Hydroxyethyl-2-pyrrolidinone, 98%, Aldrich Chemical Company, Milwaukee, Wisconsin

Polyvinylpyrrolidinone, K-30, GAF Corporation, New York, New York

1-Octyl-2-pyrrolidinone, 98%, Aldrich Chemical Company, Milwaukee, Wisconsin

1-Dodecyl-2-pyrrolidinone, 99%, Aldrich Chemical Company, Milwaukee, Wisconsin

1-Cyclohexyl-2-pyrrolidinone, GAF Corporation, New York, New York

tert-Amyl alcohol (2-methyl-2-butanol), reagent grade, Fisher Scientific Company, Fair Lawn, New Jersey

2,5-Dimethyl-2,5-hexanediol, 97%, Aldrich Chemical Company, Milwaukee, Wisconsin

2-Methoxyethyl ether, 99%, Aldrich Chemical Company, Milwaukee, Wisconsin

2-Ethoxyethyl ether, 98+%, Aldrich Chemical Company, Milwaukee, Wisconsin

Diethylene glycol dibutyl ether, 99+%, Aldrich Chemical Company, Milwaukee, Wisconsin

1,1,3,3-Tetramethyl urea, 99%, Aldrich Chemical Company, Milwaukee, Wisconsin

Succinimide, 98%, Aldrich Chemical Company, Milwaukee, Wisconsin

N-Methyl succinimide, 99%, Aldrich Chemical Company, Milwaukee, Wisconsin

Triton X-100, Rohm and Haas, Philadelphia, Pennsylvania

p-Dioxane, J. T. Baker Chemical Company, Phillipsburg, New Jersey

γ-Butyrolactone, 99+%, Aldrich Chemical Company, Milwaukee, Wisconsin

2-Piperidone (δ-Valerolactam), 99%, Aldrich Chemical Company, Milwaukee, Wisconsin

3-Methyl-2-oxazolidinone, 99%, Aldrich Chemical Company, Milwaukee, Wisconsin

1-Methyl-2-piperidone, 99%, Aldrich Chemical Company, Milwaukee, Wisconsin

Sulfolane (tetrahydrothiophene-1,1-dioxide), Eastman Kodak Company, Rochester, New York

3-Methylsulfolane (3-methyltetrahydrothiophene-1,1-dioxide), Phillips Petroleum Company, Bartlesville, Oklahoma

Diethyl malonate, 99%, Aldrich Chemical Company, Milwaukee, Wisconsin

Acryloid K-125 polymer, Lot No. 3-6326, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, Maryland

Calcium hypochlorite, 65.0% (minimum) $Ca(OCl)_2$, Bio-Lab, Inc., Decatur, Georgia

2.2 ANALYSIS OF AQUEOUS HYPOCHLORITE SOLUTIONS

The analytical procedure of ASTM Method D 2022, "Standard Test Methods of Sampling and Chemical Analysis of Chlorine Containing Bleaches," which is based on oxidation of I^- to I^0 by active $(-OCl)^-$ and subsequent titration of this I^0 with standard (0.1 N) thiosulfate solution, was initially used without modification.

In order to simplify and accelerate analysis of the data obtained, a 277-step data analysis program was prepared for a Texas Instruments TI-59 programmable calculator and printer. A typical printout from this program is presented in Figure 1. Photocopies of the printouts were placed into a project notebook for record-keeping purposes.

Data	Line No.	Item
60293.	1	Date
1645.	2	Time
3370.056	3	Sample
4.001	4	Wt, g
0.1011	5	Norm
8.4	6	1 BR
41.3	7	2 BR
32.9	8	MLT
11.79466974	9	GC/L
58.95860905	10	% ACL
23.7822585	11	GH/L
59.44078605	12	% HPC

Line 1	Date of analysis
Line 2	Time of analysis
Line 3	Sample ID No.
Line 4	Weight of HTH in grams (grams per 100-mL sample size)
Line 5	Normality of thiosulfate solution
Line 6	Initial burrett reading, mL
Line 7	Burrett reading at end point
Line 8	Milliliters of titrant used
Line 9	Grams of active chlorine per liter
Line 10	Percent of active chlorine remaining
Line 11	Grams of active HTH per liter
Line 12	Percent of active HTH remaining

Figure 1. TI-59 printout of HTH analysis.

An initial study was conducted of HTH solutions in deionized water and synthetic seawater (Carolina Biological Supply Company, Burlington, North Carolina). The results of these studies are presented in Table 1. The stability of the HTH in both deionized water and the synthetic seawater was high. An analysis of variance (AOV) of the 19 data points showed that only three isolated low-value data points were outliers (points more than 2 sigma different than the mean). The following AOV results were:

$\bar{X}$ (mean) = 71.06, the weight percent $Ca(OCl)_2$ in the bulk HTH
σ (std. dev.) = 0.648
Coefficient of deviation (CD) = 0.913%
Range ($\bar{X} \pm 2\sigma$) = 69.76% to 72.35% $Ca(OCl)_2$ by weight

With a coefficient of deviation of less than 1%, the data show that the HTH is stable in both deionized water and synthetic seawater. The mean value of 71.06% purity is acceptable as an analysis of this batch (25 lb) of HTH.

The data shown in Table 1 indicate that the synthetic seawater used in this stability study had no statistically significant effect on the stability of HTH for up to 24 hr. All tests were performed at room temperature (23° to 26°C [73° to 79°F]). As this was a synthetic seawater containing only the major and trace element salts, there was **no** organic component present.

2.3 OXIDATIVE STABILITY OF SOLVENT SYSTEMS

A laboratory test method was developed for evaluating the oxidative stability of solvent systems in concentrated aqueous hypochlorite solutions by determining the rate of hypochlorite consumption. The procedures given in ASTM Method D 2022(89), "Standard Test Methods of Sampling and Chemical Analysis of Chlorine Containing Bleaches," were utilized. The test method was developed by examination of the stability of several candidate solvent components in 4% aqueous HTH at room temperature. The concentrations of the subject solvent components were kept between 5 and 30 weight or volume percentage to ensure enough organic material was present to completely exhaust the HTH present in the overall mixture if it was reactive. The general procedure used was as follows.

Table 1. AQUEOUS SOLUTION STABILITY AND ANALYSIS OF HTH

Time (hr)	% Active HTH	g Active Cl/L	% Change in Cl content
A. HTH in deionized water, initial conc. = 7.604 g/200 mL (38.02 g/L)			
0.5	70.85	26.72	–
2.0	70.94	26.75	< 1
4.0	70.94	26.75	< 1
6.0	71.13	26.82	< 1
B. HTH in deionized water, initial conc. = 4.028 g/200 mL (20.14 g/L)			
0.5	70.86	14.16	–
2.0	71.56	14.30	+1
4.0	70.86	14.16	0
6.0	70.86	14.16	0
24.0	71.36	14.23	< 1
C. HTH in synthetic seawater, initial conc. = 8.014 g/200 mL (40.07 g/L)			
0.5	68.38	27.18	0
2.0	71.59	28.45	4.7
4.0	71.77	28.52	4.9
6.0	71.94	28.59	5.2
24.0	68.92	27.39	0.8
D. HTH in synthetic seawater, initial conc. = 4.020 g/200 mL (20.1 g/L)			
0.5	71.00	14.16	–
2.0	68.16	13.59	–4.0
4.0	71.00	14.16	0
6.0	71.00	14.16	0
24.0	71.35	14.22	< 1

1. Prepare an 8 wt % solution of HTH in deionized water ensuring that complete solution of the soluble portion of the HTH is obtained.

2. Prepare an aqueous solution (if possible) of the organic compound (10% to 60%). Heat mildly to expedite initial solution. If a positive heat of solution raises mixture temperature, cool to room temperature before going to the next step.

3. After the two solutions are stable and cooled to room temperature, mix 50-mL portions of each. Watch for heat generation and separation into two or more phases.

4. Start analysis for residual HTH within 10 min of start of mixing. Repeat HTH analysis at 0.5, 2.0, 4.0, and 6.0 hr elapsed time or until HTH concentration is less than 50% of the starting concentration.

One of the first solvents selected for determination of its stability in a 4 wt % aqueous HTH solution was *N*-cyclohexyl-2-pyrrolidinone (CHP). Two initial solutions were prepared: A was 30 mL CHP and 20 mL deionized water; B was 50 mL deionized water containing 4.0 g HTH. The two portions were combined and mixed. A stable one-phase solution was obtained. A 5-mL aliquot sample of this mixture was then added to 70 mL deionized water (following the ASTM D 2022 method); 5.0 mL glacial acetic acid was then added, followed by 2.0 g KCl. At this point the deep purple color of free iodine should be developed. (It was with all solvent candidates except CHP.) With CHP, a dark brown voluminous precipitate was formed. Apparently a water-insoluble iodine-CHP complex was formed which grossly interfered with the observation of the titration end point. Even in the presence of the soluble starch indicator, no end point could be observed.

It was found that the addition of 25 vol. % ethanol to the 70-mL diluent base produced solution of the iodine-CHP complex and color generation. Upon titration, this solution responded to addition of the soluble starch indicator and a sharp end point was observed. It was also found necessary to change the order of the addition of the 5.0-mL sample, acetic acid, and KI to the 70-mL fluid in the titrating mixture. It was observed that the sample should be added last to the water, ethyl alcohol, acetic acid, KI titrant solution to prevent oxidation of the ethanol by the HTH before reaction with the KI.

The validity of the modified ASTM D 2022 test method was checked to confirm that the procedural modification had produced no significant changes in the quality of the test results. The validity was confirmed by conducting the following series of comparative determinations. A series of three 5X replicates of 4 wt % HTH solutions in deionized water was analyzed using the 70-mL titration diluent solution of 100% deionized water, 75/25 deionized water/EtOH, and 50/50 deionized water/EtOH. Thus a total of 15 HTH purity determinations was performed. The results are presented in Table 2. It is evident from using this ethanol addition and new mixing order procedure that the results obtained are equal to the results obtained in pure water. It should also be noted that the range of these 15 values fall within the range of the previous purity determinations for the same batch of HTH.

Table 2. EFFECT OF EtOH/DI WATER TITRANT BASE SOLUTION ON HTH ANALYSIS

	Base solution		
Sample No.	100% DI water[a]	25 vol. % EtOH 75 vol. % DI water	50 vol. % EtOH 50 vol. % DI water
1	70.48[b]	70.48	71.61
2	70.48	70.03	70.03
3	70.25	70.48	70.25
4	70.48	70.48	70.71
5	69.80	70.25	70.25
X	70.30	70.34	70.56
σ	0.30	0.20	0.63
Coeff. of dev. (%)	0.43	0.28	0.89

AOV of all 15 samples

$\bar{X}$ = 70.41
σ = 0.42
Coeff. of dev. = 0.60%
Range = 69.21 to 71.61 (no outliers)

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[a] Deionized water.
[b] Data shown as wt % $Ca(OCl)_2$ in dry HTH powder.

2.4 CALCULATION OF SOLUBILITY PARAMETERS

The energy of the cohesion forces between molecules in a fluid (or solid) is dependent upon molecular structure and is equivalent to the latent heat of evaporation. These cohesive energies can be attributed to three types of attractive forces: (1) dispersive, (2) polar, and (3) hydrogen bond. The data and procedures reported by Van Krevelen (Ref. 1) were used to derive the partial (energies related to the three attractive forces) and total energy in terms of $(J)^{1/2}/(cm)^{3/2}$ where "J" is the equivalent energy in Joules and "cm" is the molar volume cm/mol. The partial and total values are used to provide numerical values related to the solvent properties of the compound(s) under study. The total energy is the square root of the sum of the squares of the three partial values. The procedures were used to select candidate solvents for investigation and for evaluating the molecular design of new synthetic products.

Key references to the major techniques for calculating solubility parameters are presented in Appendix A.

2.5 CHARACTERIZATION OF POLYMER/SOLVENT INTERACTIONS

A 100-mg sample of K-125 polymer and 5 mL of solvent were placed in a screw-cap bottle (4 cm high by 2 cm in diameter). The bottle was placed on a roller assembly and subjected to tumbling agitation for 16 hr at 25° to 27°C. The polymer/solvent mixture was observed at 30, 60, 120, 240, and 960 min. All polymer/solvent interactions (swelling, agglomeration, dissolution) were noted and the times recorded.

2.6 MELTING POINTS OF SOLVENT MIXTURES

The melting points of water/sulfolane/3-methylsulfolane mixtures were determined using the following apparatus and procedures.

The melting point tube consisted of a 6-in length of 4- x 6-mm glass tubing, one end sealed, fitted with a Type E 10-mil diameter thermocouple located 0.75 in from the tube bottom (sealed end). The mixture under test was charged to a 1 1/2-in height in the melting point tube. The filled tube was then immersed in a dry ice/Dowanol PM (propylene glycol monomethyl ether) mixture in a 500-mL dewar. Care was taken to ensure that the temperature-sensing thermocouple remained in position. The temperature of the sample was monitored by an Omega Model 650-E digital temperature indicator (in °F). This indicator has a 1-mV/°F output that was fed to an Omega Model No. 620-2M strip chart recorder. The recorder controls were set so that the recorder would indicate temperatures from 40°F (4°C) down to −60°F (−51°C) at a sensitivity of 10°F/in of chart. The chart was driven at 60 cm/hr.

The sample under test was cooled to −90° to −100°C, the tube removed and immediately placed in 3-in-thick Styrofoam block containing a 2 1/2-in-deep 0.5-in diameter hole. The sample was allowed to slowly warm to at least 32°F without being disturbed in any fashion. The rate of warming was recorded between −60° and 32°F.

The time-temperature response of this test device is a smooth hyperbolic curve, decaying if there are no melting or phase changes occurring over the operating temperature range. If melting occurs, the warming rate rapidly becomes nearly zero and produces a flat "knee" in the time-temperature response plot presented by the strip chart recorder. The true melting point can be determined by drawing a straight line through the flat "knee" of the plot and one through the response curve above the melting point (20°F range). The intercept of these two lines corresponds very well with the visual disappearance of the last solid particles in the melt, which is the normally reported melting temperature.

2.7 OXIDATIVE REACTIVITY WITH THICKENED SIMULANT

Direct measurement of the temperature of the reaction mass (50 µL of thickened simulant and 100 µL of the DAM formulation) proved to be an effective method for estimating the relative reaction rates of the formulations under study. After several trials, the following apparatus procedures were developed.

2.7.1 Apparatus

Kimax® No. 45048 6- x 50-mm culture tubes were found to be ideal for this purpose. A pair of 0.010-in diameter Teflon-insulated, "E"-type thermocouples, in "bucking" order, was prepared. One couple is the ice point reference; the other, the sample temperature detector. The output voltage from this couple pair was amplified (Texas Instruments TL082 dual operational amplifier based gain unit) 294 times to provide an output of 10 mV/°F (18 mV/°C). This sensitivity was within a ±0.5% accuracy limit between the temperatures of 70° and 85°F (21.1° and 29.4°C). The temperature-proportional voltage was fed to the input of an Omega Model No. 620 2M 10-in strip chart recorder. When set on the 100-mV sensitivity range, this arrangement provided a range of 10°F at 1.0°F/in of chart width at a readable sensitivity of ±0.05°F. This range was ideal for this purpose as trial runs had shown that temperature increases of 4° to 8°F were to be expected using the culture tube reaction with the 50/100-µL sample size.

2.7.2 Procedure

Fifty microliters (0.05 mL) of the K-125 thickened diethyl malonate agent simulant was charged into the bottom of the culture tube using a 1-cc insulin syringe and a 2-in-long, 18-gauge needle. Care was taken to ensure that all the simulant was placed in the bottom of the culture tube with none smeared on the side of the tube. Six or seven tubes were loaded for use in each evaluation of a single batch of DAM formulation. Sample tubes were handled with forceps to prevent addition of heat from handling. Each tube was placed in a holder consisting of 2-in-thick polystyrene foam containing 1/4-in holes (bored with a cork borer). The samples were held there until needed. After standing in the holders for 30 min (for temperature equilibrium with room conditions), a single tube was then placed into a test holder consisting of a 2-in cube of Styrofoam with a 1 1/2-in-deep, 1/4-in diameter hole. The sample "E" thermocouple was then inserted into the culture tube so that the thermocouple weld bead was contacting the center bottom of the tube. The other thermocouple junction was immersed in a water-ice mixture in a glass dewar to provide a 32°F (0°C) reference. The chart recorder pen was adjusted to plot the test sample temperature on the 1-in line above chart zero and the chart drive started. The sample in the 2-in cube holder was then tilted about 30 degrees off vertical, and 100 µL (0.10 mL) of the DAM formulation under study was slowly injected down the culture tube so that it washed gently over the surface of the thickened simulant. A 1-mL insulin syringe with a 1-in, 18-gauge needle was used to inject the DAM formulation. The reaction starts within 2 or 3 sec as indicated by an increase in sample temperature. The sample temperature was recorded until the peak temperature was reached, and 0.5°F cooling from this maximum was observed. The chart drive was turned off at this point and the recording pen lifted from the chart. The sample-sensing thermocouple was then removed from the culture tube, washed first in water and then in acetone, and dried. The chart drive was operated at 3 cm/min. A typical reaction time/temperature plot is shown in Figure 2. The total reaction times ranged from 3 to 4 min. Three data points were extracted from each time/temperature plot as follows:

1. <u>Maximum Temperature Rise</u>

   Measure (in inches) the vertical distance from the start line to the peak of the plot. Multiply this value by 10°F/in to calculate the temperature rise.

2. <u>Reactivity Rate Index</u>

   Draw a straight line from the start point (where temperature rise first occurs) to a point on the plot corresponding to one-half (1/2) of the total peak height from the start line. Calculate the slope of this line in terms of °F/min. This slope is an index of the speed of heat release, thus the reaction rate.

3. <u>Time to Maximum Temperature</u>

   Measure the distance (in cm) on the longitudinal length of the chart plot from the start to the point corresponding to the peak temperature. Multiply this value by 20 sec/cm to obtain the time, in sec, to maximum temperature. This value is also an indirect measure of reaction rate.

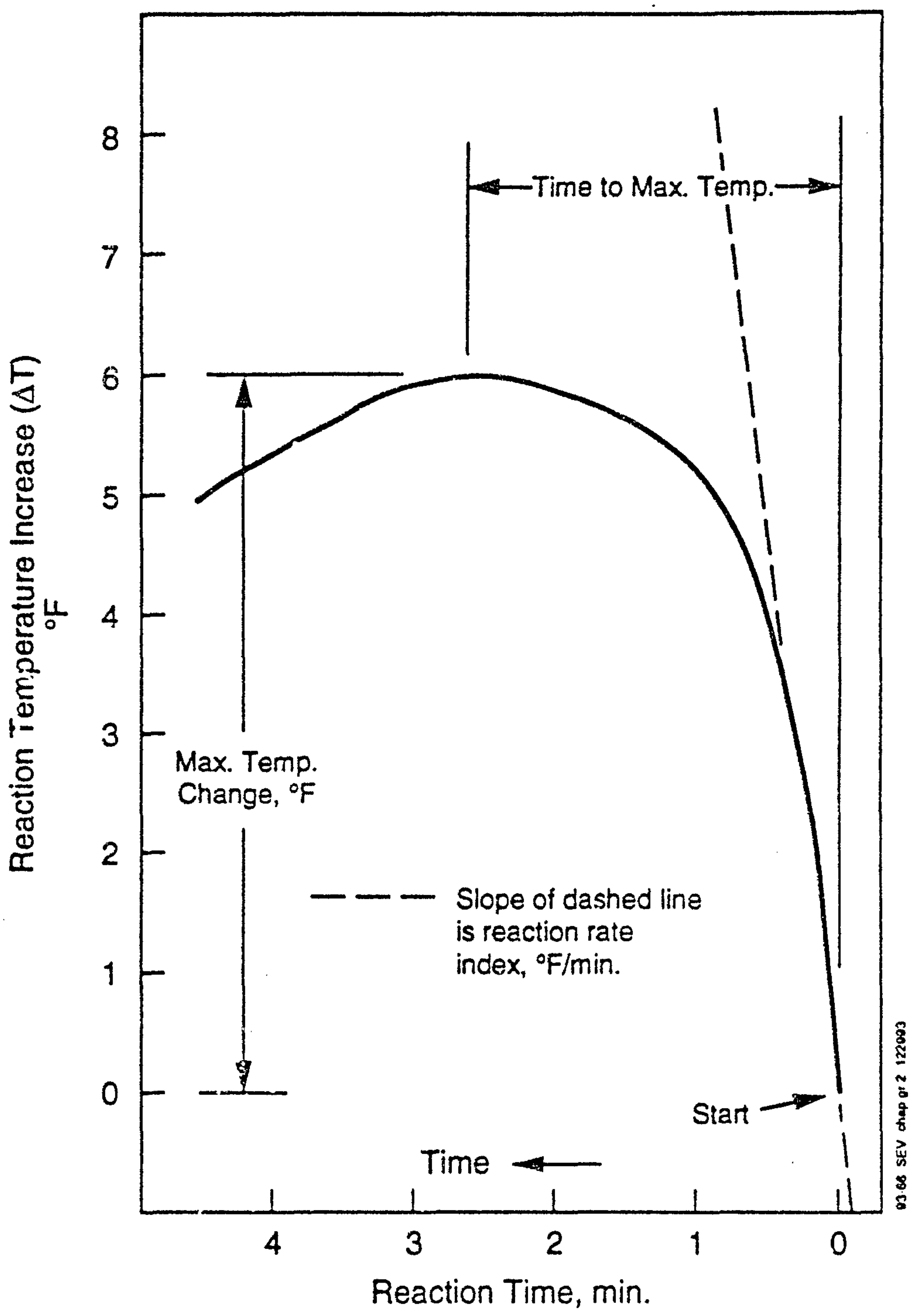

Figure 2. Reaction time/temperature plot for reaction of sulfolane DAM formulation with thickened agent simulant.

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SECTION 3

RESULTS AND DISCUSSION

The experimental results obtained during the course of this exploratory development program are presented and discussed in this section.

3.1 SELECTION OF CANDIDATE SOLVENT SYSTEMS

Review and analysis of pertinent information obtained from ERDEC communications, literature surveys (see Appendix A), and industrial contacts (see Appendix B) provided the basis for a general approach to solvent selection.

- The organic solvent components must be relatively stable to oxidative attack by hypochlorite. An effective pot life of at least 6 h is required of the DAM composition. The molecular structure of the organic components must be such that there are no or only very limited readily oxidizable reactive groups (i.e., tertiary hydrogens, readily oxidizable hydroxy groups, aldehydes and the like).

- The major components of a suitable DAM system must consist of a highly polar, aprotic organic solvent similar in properties to the *N*-cyclohexyl pyrrolidinone that has been previously investigated. The molecular weight of this solvent must be sufficiently high to limit its vapor pressure and subsequent flash point to 110°F (43°C) as a minimum.

- Ancillary compounds such as surfactants (i.e., Triton X-100) and couplers (i.e., tertiary butyl alcohol, TBA) must have similar vapor pressure and flash point properties. In addition, these compounds must be completely miscible in fresh and sea waters.

- Control of the balance of the three complex solubility parameters ($\delta_T = [(\delta_d)^2 + (\delta_p)^2 + (\delta_h)^2]^{1/2}$) must be maintained to control solubility properties.

- The solubility parameter values of the solvent will define its ability to form a stable, one-phase solution of the solvent, water, the ancillary compounds and the calcium hypochlorite (HTH).

The complex solubility parameters for the K-125 polymeric thickening agent and a series of *N*-substituted pyrrolidinones, pyrroles, and succinimides were calculated to provide a basis for selection of promising solvents. The techniques for calculating these values were based on those described by D. W. Van Krevelen (Ref. 1), who developed an equation that utilizes the complex parameters of both solvent and polymer to develop a $\overline{\Delta\delta}$ (difference in mean solubility parameters) value as follows:

$$\overline{\Delta\delta} = \left[(\delta_{d,P} - \delta_{d,S})^2 + (\delta_{p,P} - \delta_{p,S})^2 + (\delta_{h,P} - \delta_{h,S})^2\right]^{1/2}$$

where: $\delta_{d,P}$ = dispersion force contribution to the polymer $\delta_{T,P}$

$\delta_{d,S}$ = dispersion force contribution to the solvent $\delta_{T,S}$

and so on for the polar and hydrogen bonding components.

$$\delta_{T,P} = \left[(\delta_{d,P})^2 + (\delta_{p,P})^2 + (\delta_{h,P})\right]^{1/2} \qquad \text{and}$$

$$\delta_{T,S} = \left[(\delta_{d,S})^2 + (\delta_{p,S})^2 + (\delta_{h,S})^2\right]^{1/2}$$

For good solubility of a polymer in a solvent, the mean solubility parameter difference should be equal to or less than 5 (≤ 5). These relationships provide a convenient method for estimating the solvent's potential.

The K-125 polymer used as an agent thickener is a mixture of methylmethacrylate (MMA), *n*-butylmethacrylate (nBuMA), and *n*-propylmethacrylate (nPrMA) homo polymers. The calculated (Ref. 1) complex solubility parameters for these three polymers are shown in Table 3.

Table 3. COMPLEX SOLUBILITY PARAMETER FOR K-125 POLYMER

Polymer	ρ, g/cc	Molar volume, cc	δ_d	δ_p	δ_h	δ_T
PMMA	1.17	86.5	16.5	5.7	9.0	19.7
PnPrMA	1.08	118.7	16.6	4.1	7.7	18.8
PnBuMA	1.05	135.2	16.6	3.6	7.2	18.4
1:1:1 mix of above	1.10	113.5	16.6	4.4	8.0	18.9

The 1:1:1 mix ratio is an assumption as the ratio was not known at the time these calculations were made. However, as the complex solubility parameters of these three polymers are quite similar ($\overline{\Delta\delta}_{max} = 2.8$), changes in the mix ratios would have very little affect on solubility characteristics.

Calculation of the $\overline{\Delta\delta}$ value between the K-125 mix for diethylmalonate and cyclohexylpyrrolidinone (CHP) yielded values of 2.8 and 3.1, respectively. The ready solubility of K-125 polymer in these two solvents has been repeatedly demonstrated in the past. These observations validate this theoretical method for estimating the potential of a model solvent for dissolving the K-125 polymeric thickening agent.

The complex solubility parameters calculated for the *N*-substituted pyrrolidinones, an *N*-substituted pyrrole, an *N*-substituted succinimide, and two sulfolanes are presented in Table 4. The methyl-capped ethylene oxide adducts look quite interesting. They retain the same solubility parameters with increasing molecular weight, a highly desirable property for control of flash point and perhaps skin and eye irritation problems. The *N*-substituted succinimide compound has very high polar and hydrogen bonding parameters, which makes it an interesting solvent class if its other physical properties were appropriate.

Table 4. COMPLEX SOLUBILITY PARAMETERS FOR SELECTED SOLVENTS

(δ IN $J^{1/2}$ / $cm^{3/2}$)

Compound	δ_d	δ_p	δ_h	δ_T
A. *N*-Pyrrolidinones				
1. *N*-Methyl	17.4	11.4	8.3	22.2
2. *N*-Cyclohexyl	18.0	6.8	6.6	20.3
3. *N*-$(C_2H_4O-)CH_3$	17.5	8.7	8.6	21.3
4. *N*-$(C_2H_4O-)_2CH_3$	17.5	8.0	8.7	21.1
5. *N*-$(C_2H_4O-)_3CH_3$	17.6	7.9	8.8	21.2
6. *N*-$(C_2H_4O-)_4CH_3$	17.6	8.0	8.8	21.3
7. *N*-C_2H_4OH	16.9	11.0	15.6	23.2
8. *N*-$(C_2H_4O-)_3H$	17.0	8.0	13.4	23.3
9. *N*-Dodecyl	16.1	3.8	4.9	17.2
B. *N*-$(C_2H_4O-)H$ pyrrole	16.2	6.8	8.2	19.3
C. *N*-Methylsuccinimide	17.4	13.4	9.5	23.9
D. Sulfolanes				
1. Sulfolane	17.6	19.7	7.6	27.5
2. 3-Methylsulfolane	17.9	16.6	7.0	25.4

3.2 OXIDATIVE STABILITY OF SELECTED SOLVENTS

The 6-hr stability of selected solvents in an aqueous solution containing 4 wt % hypochlorite was determined for some 40 solvents and solvent mixtures. Oxidation of the solvent was followed by monitoring the level of active chlorine in the test mixture. The results ranged from near instantaneous oxidation to less than 4% loss of available chlorine after 6 hr exposure. A complete summary of the test results is presented in Tables C-1 through C-3 and in Figures C-1 through C-9 in Appendix C.

Those solvents showing better than 60% retention of available hypochlorite are presented in Table 5 and Figure 3. The reference solvent 1-cyclohexyl-2-pyrrolidinone (CHP) is the least oxidatively stable of the liquid solvents. The alcohols were rejected because they are not solvents for the K-125 polymeric thickener. The only potential solvents to replace the 1-cyclohexyl-2-pyrrolidinone were sulfolane and 3-methylsulfolane. It is interesting to note that *t*-butyl alcohol exhibited the highest resistance to oxidation by aqueous hypochlorite of all the solvents examined. This stability probably reflects the shielding effect of the three methyl groups around the hydroxyl functionality.

The two sulfolanes are excellent candidates for use in the DAM formulation. In addition to their superior oxidative resistance, both compounds have very low vapor pressure (< 1 torr) over the temperature range of 0° to 60°C (32° to 140°F). The boiling points of the sulfolanes are above 200°C at 1 atm, and a mixture of the two compounds can have a melting point as low as −15°C (5°F) with an usable fluid range. The limited toxicological data (Ref. 2) shows that the compounds have low acute toxicity and are only mildly irritating to the skin and eyes. Their compatibility with chemical agent monitors (CAMs) is unknown. The very low vapor pressure of these compounds suggests that they may have only a very limited impact. These two compounds are typical of aprotic, strongly polar high boiling solvents.

Table 5. STABILITY OF STABLE SOLVENTS IN 4% AQUEOUS HTH

	Percent of original HTH at indicated time[a]				
Solvent	0 hr	0.5 hr	2 hr	4 hr	6 hr
t-Butyl alcohol	101.2	100.1	101.2	100.4	ND
N-Cyclohexylpyrrolidinone	94.5	91.9	89.0	86.6	83.7
2,5-Dimethyl-2,5-hexanediol	89.9	83.9	85.2	85.0	ND
Sulfolane	97.5	96.4	95.8	94.9	94.6
3-Methylsulfolane	94.8	94.2	94.2	93.5	92.9

[a] Concentration of hypochlorite in water control at 0 hr = 100%.

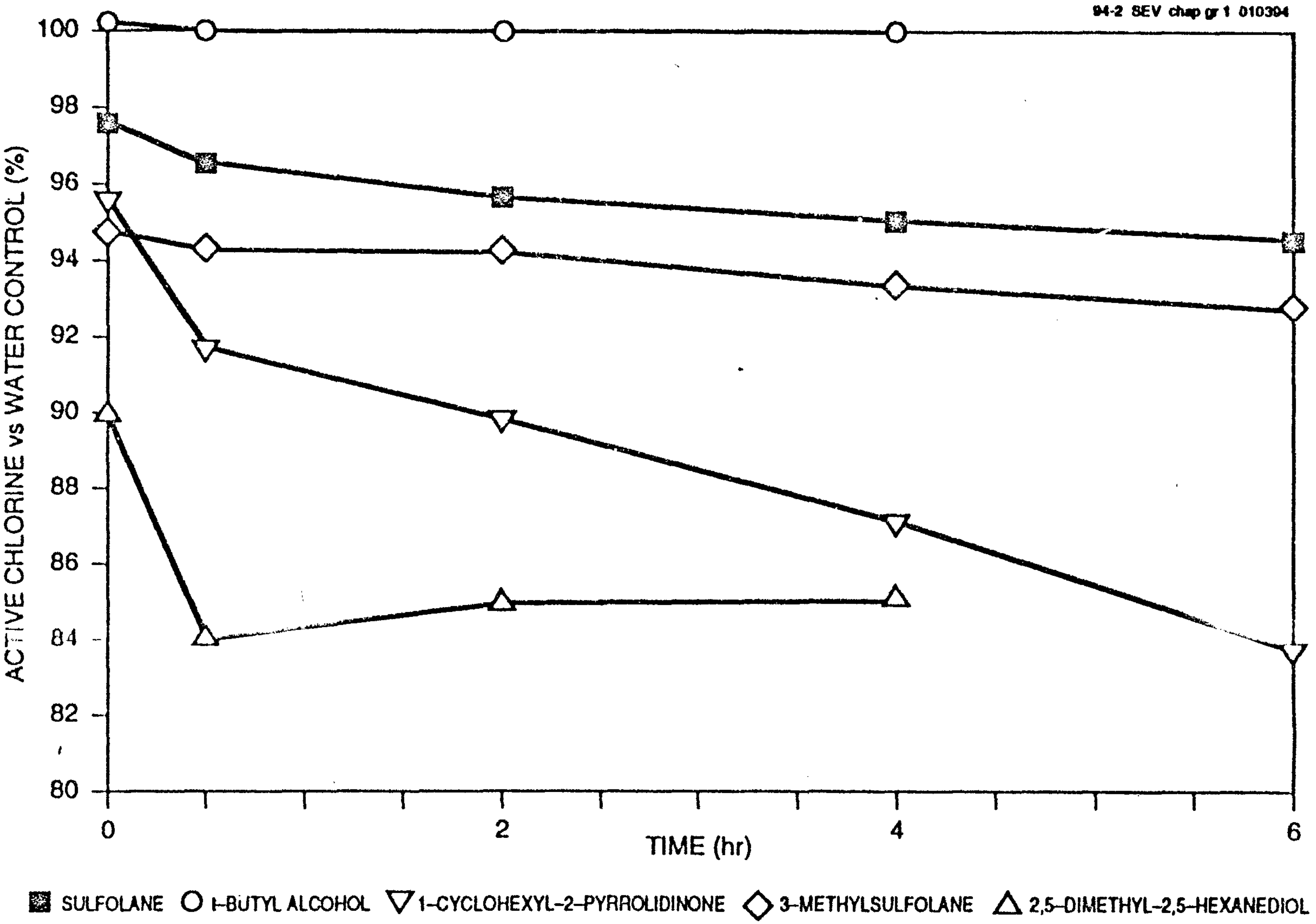


Figure 3. Stability of most stable solvents in aqueous hypochlorite solution.

3.3 PYRROLIDINONE-BASED SOLVENT SYSTEMS

The oxidative stability of the following seven pyrrolidinones was evaluated using the standard aqueous hypochlorite test: (a) 2-pyrrolidinone (2-P), (b) poly-*N*-vinyl-2-pyrrolidinone (PNVP), (c) 1-methyl-2-pyrrolidinone (NMP), (d) 1-cyclohexyl-2-pyrrolidinone (CHP), (e) 1-hydroxyethyl-2-pyrrolidinone (2'-HE-2-P), (f) 1-octyl-2-pyrrolidinone (NOP), and (g) 1-dodecyl-2-pyrrolidinone (DDP). The results of the tests of the five water-soluble pyrrolidinones are shown in Figure 4, and the results for the two partially soluble pyrrolidinones, NOP and DDP, are shown in Figure 5.

Only CHP exhibited sufficient oxidative stability to meet the DAM stability requirement, i.e., retention of > 6[illegible]% of the hypochlorite content 4 hr after mixing. All other pyrrolidinones failed to possess the desired stability and/or solubility requirements. Therefore, it appeared that formulation studies and/or synthetic designs would be required to achieve the desired physicochemical properties.

3.3.1 Formulation Studies with *N*-Alkyl-2-pyrrolidinones

N-Octyl- and *N*-dodecyl-2-pyrrolidinone showed very limited solubility in aqueous solution as reflected by their low solubility parameters. A series of formulations was made using either *t*-butanol or 2,5-dimethyl-2,5-hexanediol as a cosolvent to aid in increasing water solubility. Only modest increases in the solubility of water in these two pyrrolidinones were created by the cosolvents. For example, neat *N*-octyl-2-pyrrolidinone (NOP) will dissolve 0.45 mL water per mL before phase separation.

A 25 wt % solution of 2,5-dimethyl-2,5-hexanediol in *N*-octyl-2-pyrrolidinone would dissolve 0.55 mL water before phase separation occurred. Similar but smaller amounts of water were soluble in *N*-dodecyl-2-pyrrolidinone (DDP) and cosolvent mixtures. Under no conditions was it found possible to prepare stable-water NOP or DDP solutions with cosolvents that would remain in a single-phase state if there was 1% or more HTH in the water portion. Phase separation occurred almost instantaneously on addition of HTH. Water dissolved in the pyrrolidinone solvent, even with highly polar cosolvents, cannot support the solution of the ionic HTH.

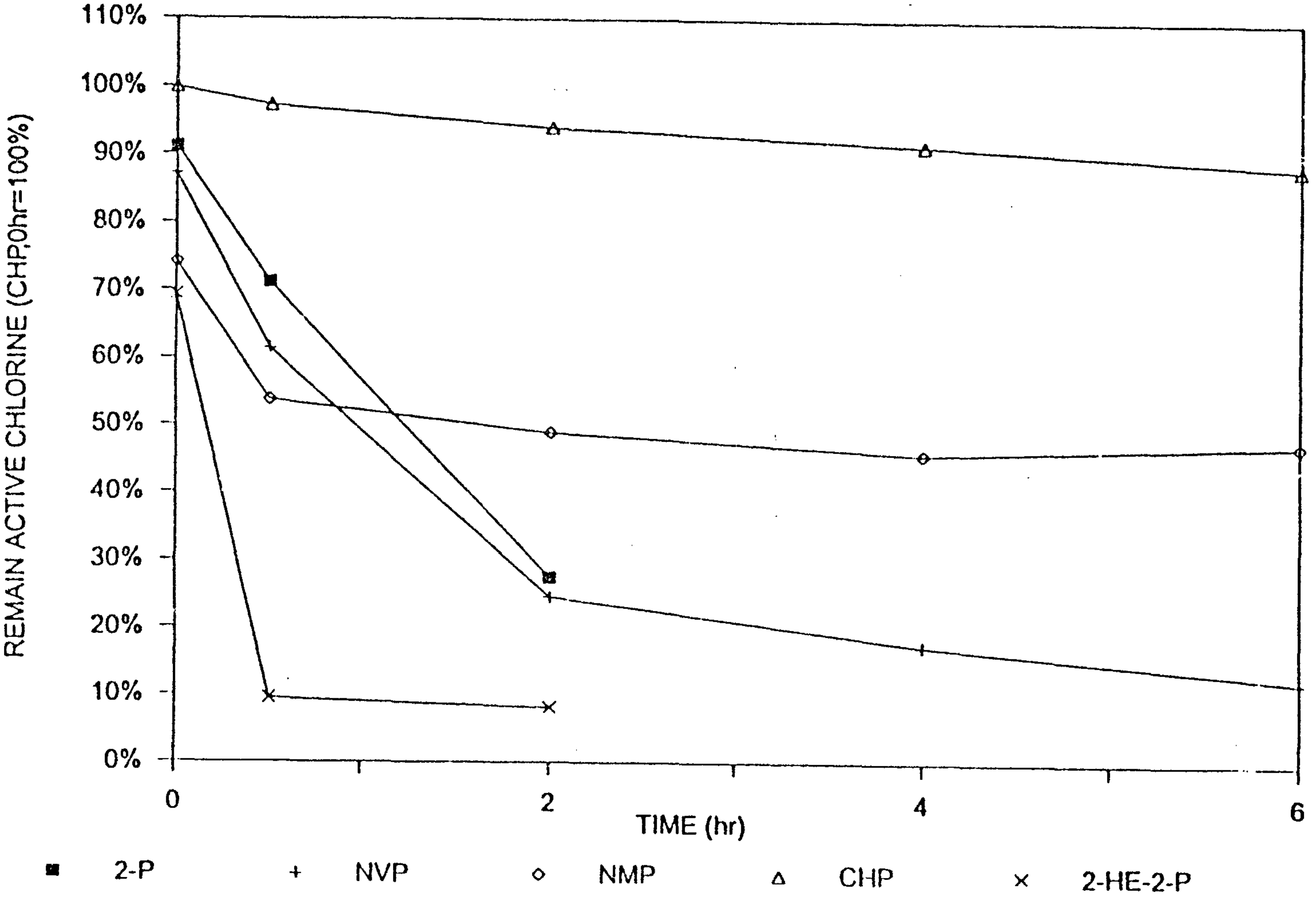


Figure 4. Oxidative stability of soluble pyrrolidinones.

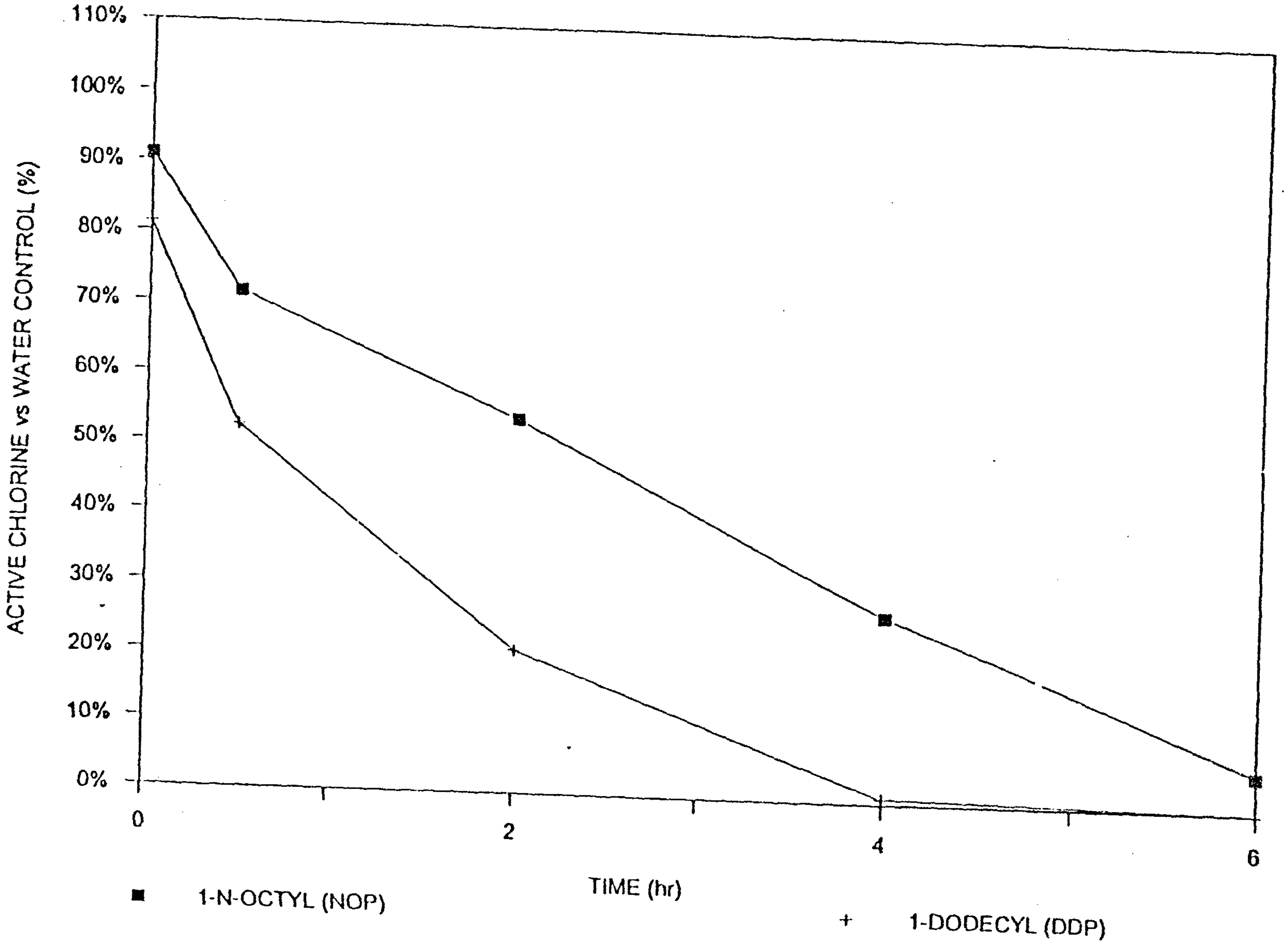


Figure 5. Oxidative stability of partially soluble pyrrolidinones.

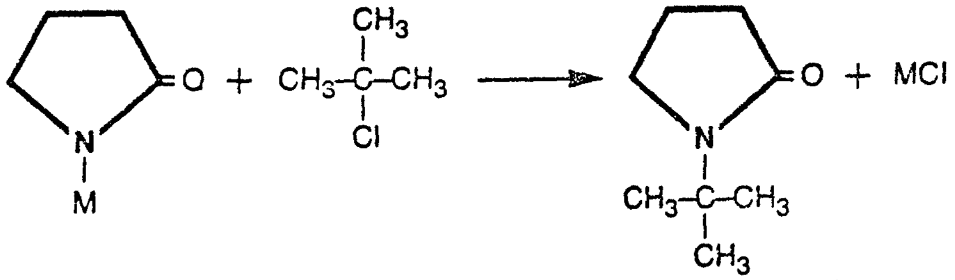
Attempts to prepare water-based solutions of these two pyrrolidinones all met with failure in the presence of any substantial volume of water (> 50 vol %), and also failed if more than 1% HTH (by weight based on water content) was present. The data shown in Figure 5 are based on a two-phase system kept under constant stirring with a magnetic mixer. These results show that neither of these pyrrolidinones have much stability in the presence of HTH. Further work with these solvents was abandoned.

3.3.2 Design and Synthesis of Stable Pyrrolidinones

Two oxidatively stable pyrrolidinone structures were designed for synthesis and evaluation studies: (a) 1-*t*-butyl-2-pyrrolidinone and (b) 1-[2(2,5-dimethyl-5-hydroxyhexyl)]-2-pyrrolidinone. The rationale for the structural designs and proposed synthetic routes are presented as follows:

3.3.2.1 1-*t*-Butyl-2-pyrrolidinone

Review and analysis of the oxidative stability test data presented in Table C-1 of Appendix C indicate that structural steric hindrance of the oxidizable entity (i.e., the –OH group of *t*-butanol and 2,5-dimethyl-2,5-hexanediol, and the cyclohexyl ring placement on the N atom of pyrrolidinone) provides protection from oxidation. This consideration provided the basis for designing an oxidatively stable group to replace the cyclohexyl ring. Such a group could be tailored to provide the desired complex solubility parameters. The fair stability of *N*-methyl-2-pyrrolidinone is a good example of the shielding effects. A tertiary butyl group on the pyrrolidinone nitrogen should provide enhanced oxidative stability. This compound, 1-*t*-butyl-2-pyrrolidinone, has been reported in the literature (Refs. 3-5). Its synthesis used the same high-pressure (50 to 200), high-temperature (250° to 280°C) gas phase reaction used to produce the cyclohexyl derivative. The starting materials were 2-amino-2-methylpropane (*t*-butylamine) and γ-butyrolactone. Since no commercial source could be identified, the synthesis of this compound was attempted by the reaction of selected salts of 2-pyrrolidinone with *t*-butyl chloride as represented by the following equation:



Where: M = Li, Na or K

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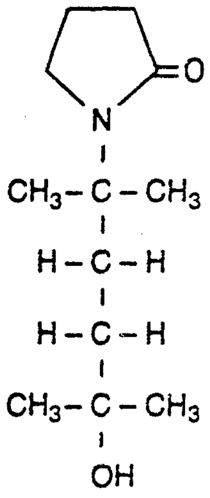
The synthetic procedures and results are reported in detail in Appendix D.

3.3.2.2 1-[2(2,5-Dimethyl-5-hydroxyhexyl)]-2-pyrrolidinone

The stability of CHP over a 6-hr period is sufficient to meet goal requirements, but this material is a corneal irritant and in addition appears to "foul" the chemical agent monitor, greatly reducing its (the detector's) usefulness. It is quite interesting to note (from GAF data sheet) that 1-(2-hydroxyethyl)-2-pyrrolidinone is only a minimal irritant. An explanation of this behavior would be of value. However, the hydroxyethyl pyrrolidinone has very low oxidative stability.

A compound of particular interest is 2,5-dimethyl-2,5-hexanediol. This diol has very good resistance to oxidation by $Ca(OCl)_2$. Its structure is essentially a dimer of tertiary butanol, which is also very oxidatively stable. These observations suggest that a solvent molecule containing the diol structure as an *N*-substituted group on the pyrrolidinone ring might have all the required properties including insensitivity to the chemical agent monitor because its molecular weight is substantially higher than CHP. The molecular structure of the proposed solvent is:



1-[2(2,5-Dimethyl-5-hydroxyhexyl)]-2-pyrrolidinone

The calculated solubility parameters are: $\delta_d = 16.0$; $\delta_p = 5.7$; $\delta_h = 11.3$; and $\delta_T = 20.4$.

The $\overline{\Delta\delta}$ between this solvent and the 1:1:1 K-125 mixture was found to be 3.6 which is well within the good solvent (≤ 5) range. This proposed solvent would be a good subject for future synthesis work.

3.4 SULFOLANE-BASED SOLVENT SYSTEMS

The excellent resistance of sulfolanes to degradation and reaction in aqueous HTH solution (see Figure 6) and the near complete solubility of K-125 in these solvents dictated that these solvent systems be subject to a detailed evaluation for their suitability as a DAM base solvents. The advanced developmental work was focused on studies of sulfolane (tetrahydrothiophene-1,1-dioxide), 3-methylsulfolane (3-methyl tetrahydrothiophene-1,1-dioxide), binary mixtures of these sulfolanes, and ternary mixtures of the two sulfolanes plus water. The developmental studies were structured to define three important parameters of the sulfolane-based solvent systems: (a) solvation of K-125 polymer, (b) freezing point/composition relationships, and (c) reactivity with thickened simulant.

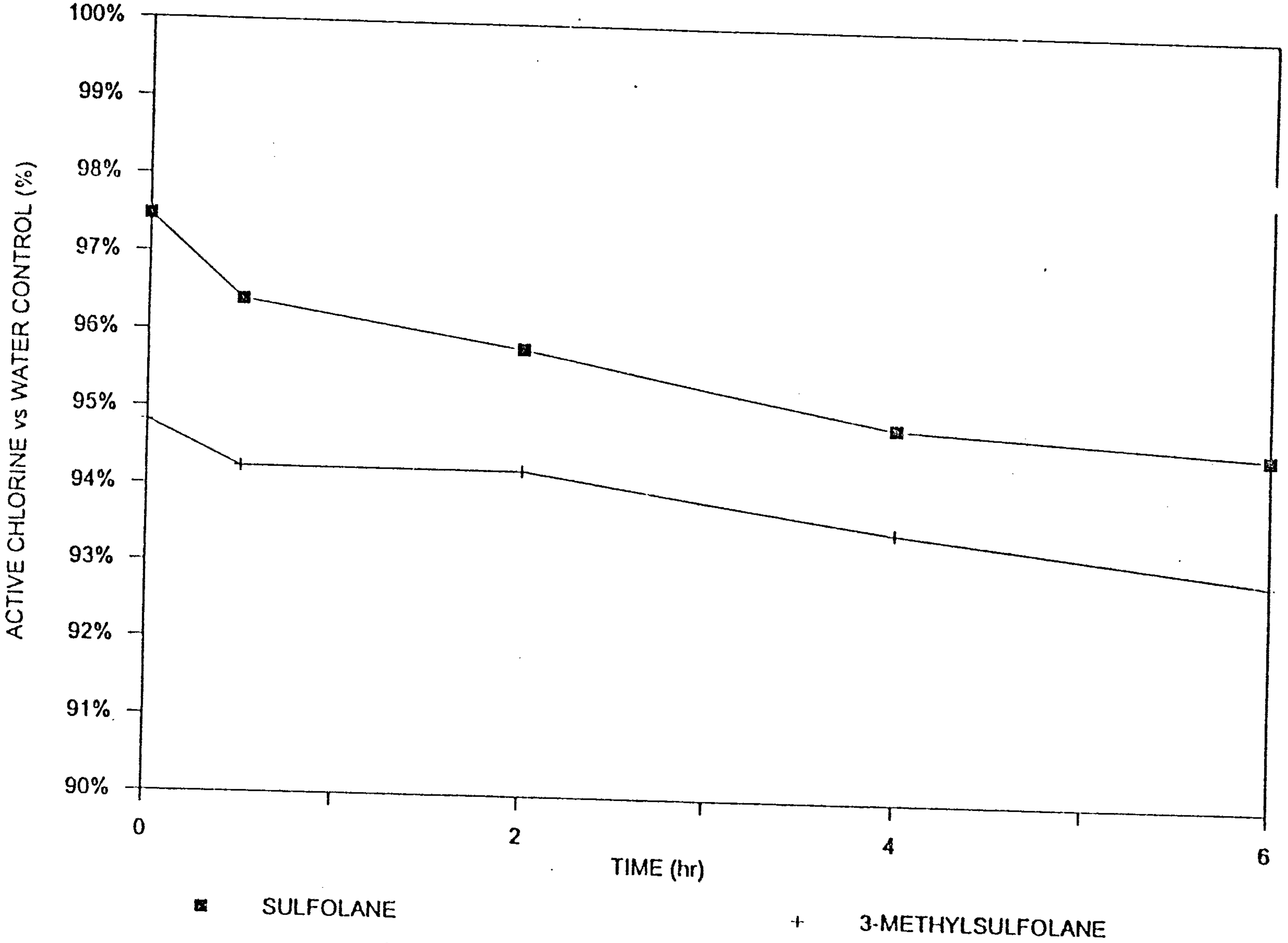


Figure 6. Oxidative stability of sulfolanes.

3.4.1 Solvation of K-125 Polymer

Sulfolane was found to be a "near" solvent for the acrylic thickener, K-125, at a 5 wt % concentration. On mixing, the polymer powder was initially highly swollen, and then, in 24 hr, a cloudy solution was obtained. This solution, however, was unstable and reverted to a two-phase mass consisting of a relatively low viscosity fluid and a thick, rubbery gel phase. This separation occurred 72 hr after mixing on standing at room temperature. Apparently, the high solubility parameter ($\delta_T = 27.5\ J^{1/2}/cm^{3/2}$) prevented complete solution. The formation of a gel structure suggests that only very high swelling of the polymer mixture occurs in sulfolane.

The insertion of a single methyl group onto the three (3) position of the tetrahydrothiophene-1,1-dioxide molecule made a substantial change in solubility. The K-125 polymer dissolved as fast in 3-methylsulfolane as it did in diethyl malonate and *N*-cyclohexyl-2-pyrrolidinone, less than 16 hr under tumbling agitation. The solution obtained was a crystal-clear, color-free, viscous fluid exhibiting stringy flow. It was apparent that 3-methylsulfolane was an excellent solvent for the K-125 thickening agent.

An examination of the interaction with K-125 powder with three solvents, *N*-cyclohexyl-2-pyrrolidinone (the reference solvent), sulfolane, and 3-methylsulfolane in aqueous (35 vol % solvent) solution showed very interesting results. Nearly immediate swelling of the K-125 polymer powder (0.1 g in 5 mL of solvent/water mixture) particles was observed with all three solvent/water mixtures. It was obvious within 30 min that the 3-methylsulfolane solution was causing the most rapid swelling of the polymer powder. After 2-hr exposure time, the particles in the pyrrolidinone and sulfolane solutions were notably increased in size (2 to 3X) with no evidence of particle agglomeration. Particles in the 3-methylsulfolane were sticking to each other and were highly swollen. On standing overnight (16 hr), the polymer particles in the *N*-cyclohexyl-2-pyrrolidinone and sulfolane were more swollen (≅ 5X) but were not agglomerated. Swelling effects in these two water-solvent mixtures were essentially equal. Swelling and agglomeration in the 3-methylsulfolane/water mixture were substantially higher.

The high swelling of the K-125 polymer particles in the aqueous 3-methylsulfolane solution suggests that 3-methylsulfolane would be the superior

DAM solvent of the three investigated. Such swelling should ensure that the 3-methylsulfolane would rapidly penetrate the thin skin of polymer found on an agent droplet even when in an aqueous solution containing HTH. The ability to rapidly penetrate a thickened agent droplet under these conditions should lead to faster and more complete decontamination.

3.4.2 Melting Point/Composition Relationships

The two sulfolanes, 3-methylsulfolane and sulfolane, have rather high melting points when pure, −2° and 27°C, respectively. Commercially available liquid sulfolane is marketed with 3 to 5 vol % water, which lowers the freezing point to ≅ 7°C (45°F). The effect of water content in sulfolane on the mixture freezing point is shown in Figure 7. At 10% water, the freezing point is 0°C (32°F). The melting points of mixtures of sulfolane and 3-methylsulfolane have been reported by Shell International Chemical Company Ltd. (see Figure 8). Mixtures of 3-methylsulfolane containing between 42 mol % (45 wt %, 46.9 vol %) and 65 mol % (67 wt %, 68.7 vol %) 3-methylsulfolane show a melting point minimum in the −15° to −17°C (5° to 2°F) range.

A low melting point (≅ −30°C [−22°F]) component "A" (the organic solvent[s]) of the DAM formulation is one of the required properties. The amount of water required to produce maximum freezing point depression in the 60 vol % (58.6 wt %, 55.9 mol %) 3-methylsulfolane, 40 vol % (41.4 wt %, 44.1 mol %) solvent mixture was determined.

Nine mixes of 60/40 vol % 3-methylsulfolane/sulfolane containing from 1.2 to 25 vol % water were prepared. The melting temperature of each mixture was determined in triplicate using the apparatus and procedure described in Section 2.6. The mean of the three determinations was recorded as the melting point. Figure 9 presents a typical melting point determination time-temperature plot. The minimum melting temperature occurred at a water content of 11.0 vol % with a mean melting point of −25°C (−13°F) as shown in the plot of water content versus melting temperature shown in Figure 10.

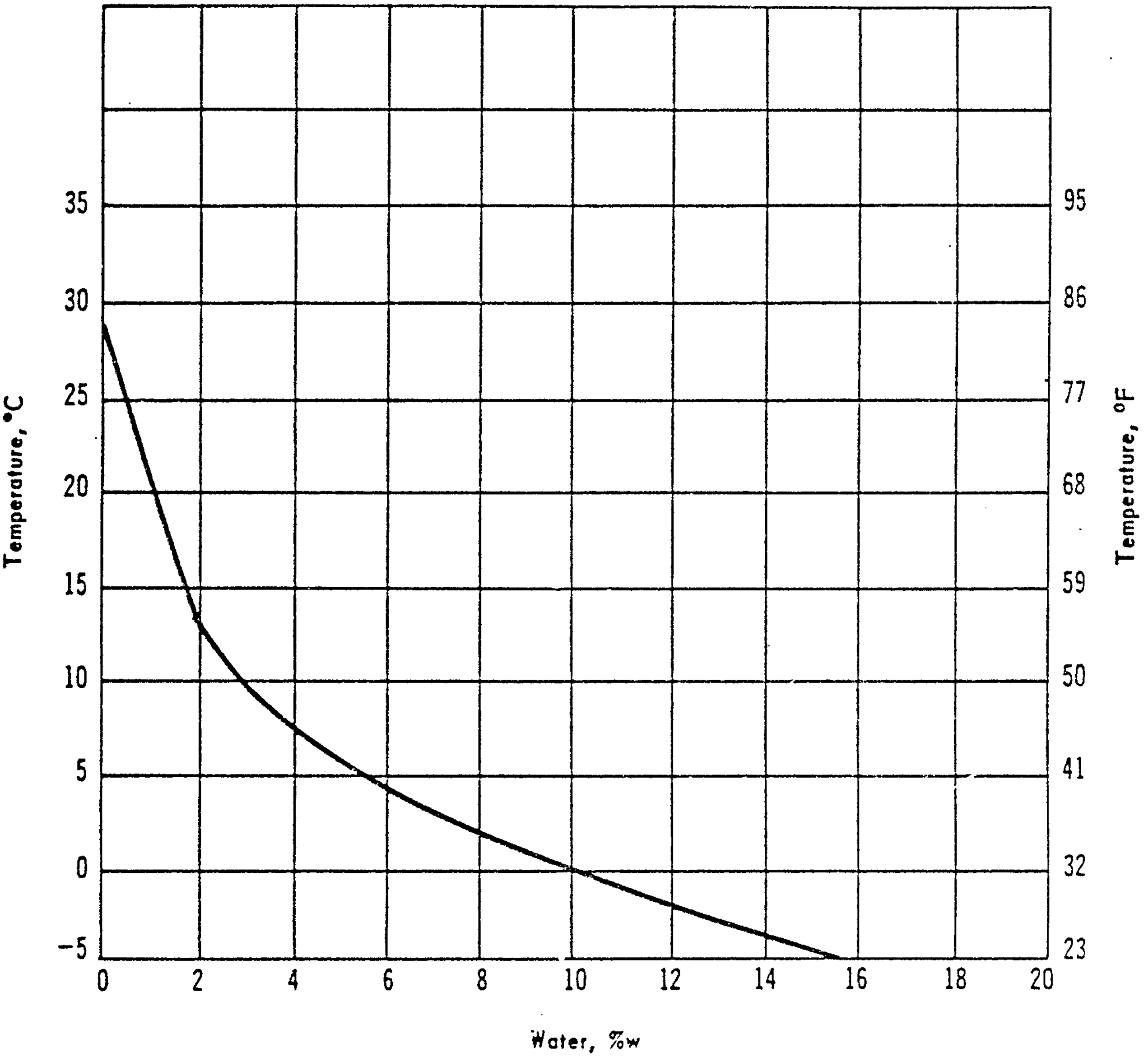


Figure 7. Melting point of sulfolane/water mixtures.

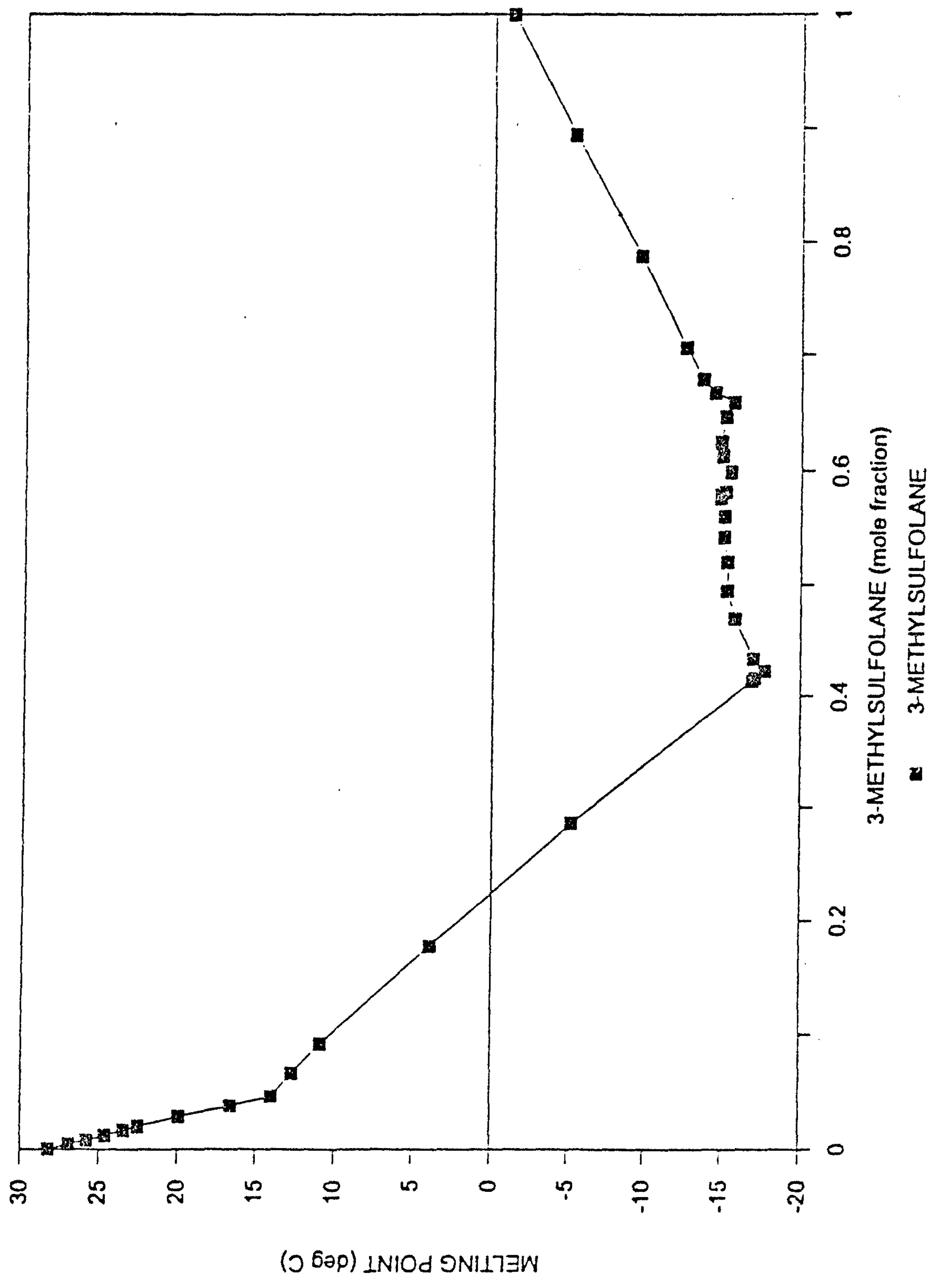


Figure 8. Melting point of sulfolane/3-methylsulfolane mixtures.

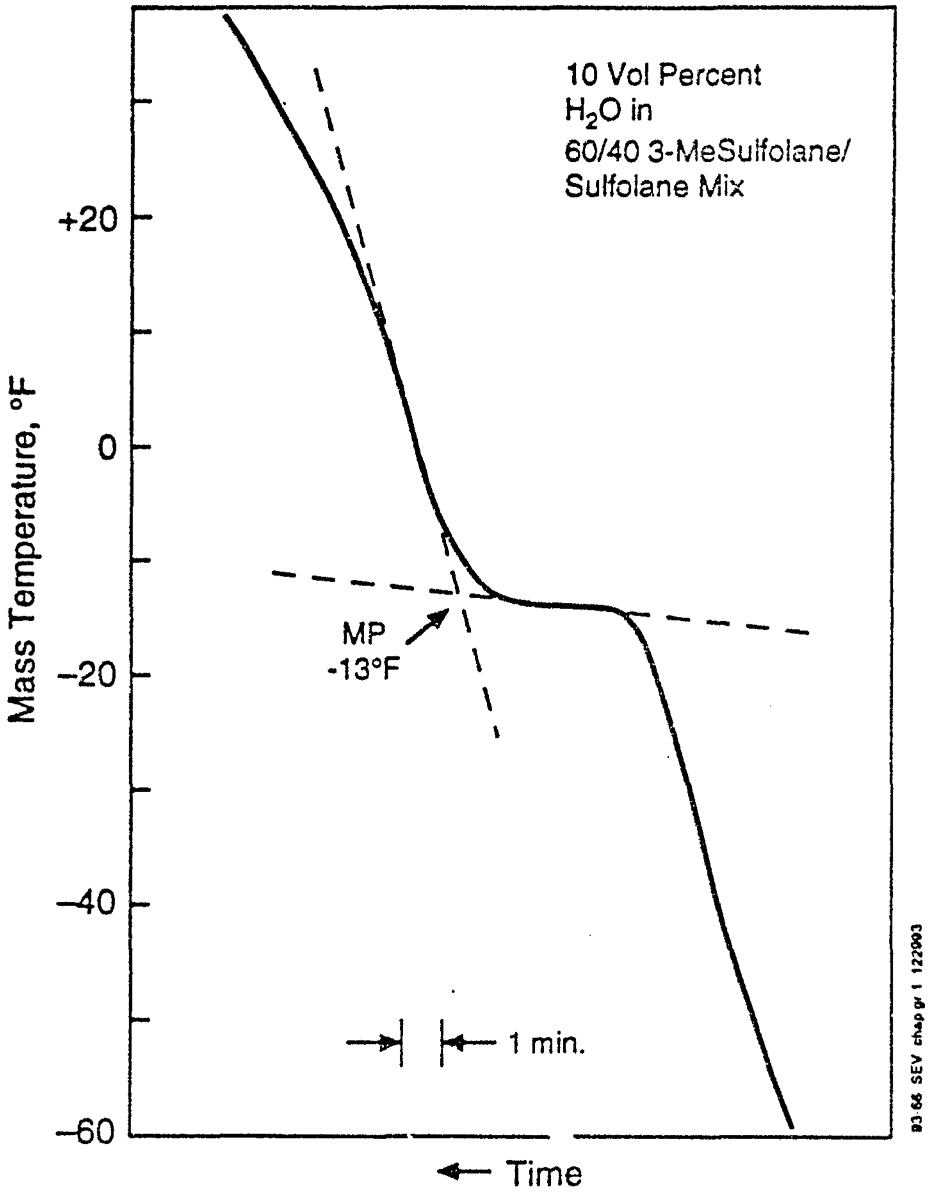


Figure 9. Typical melting point determination: time/temperature plot.

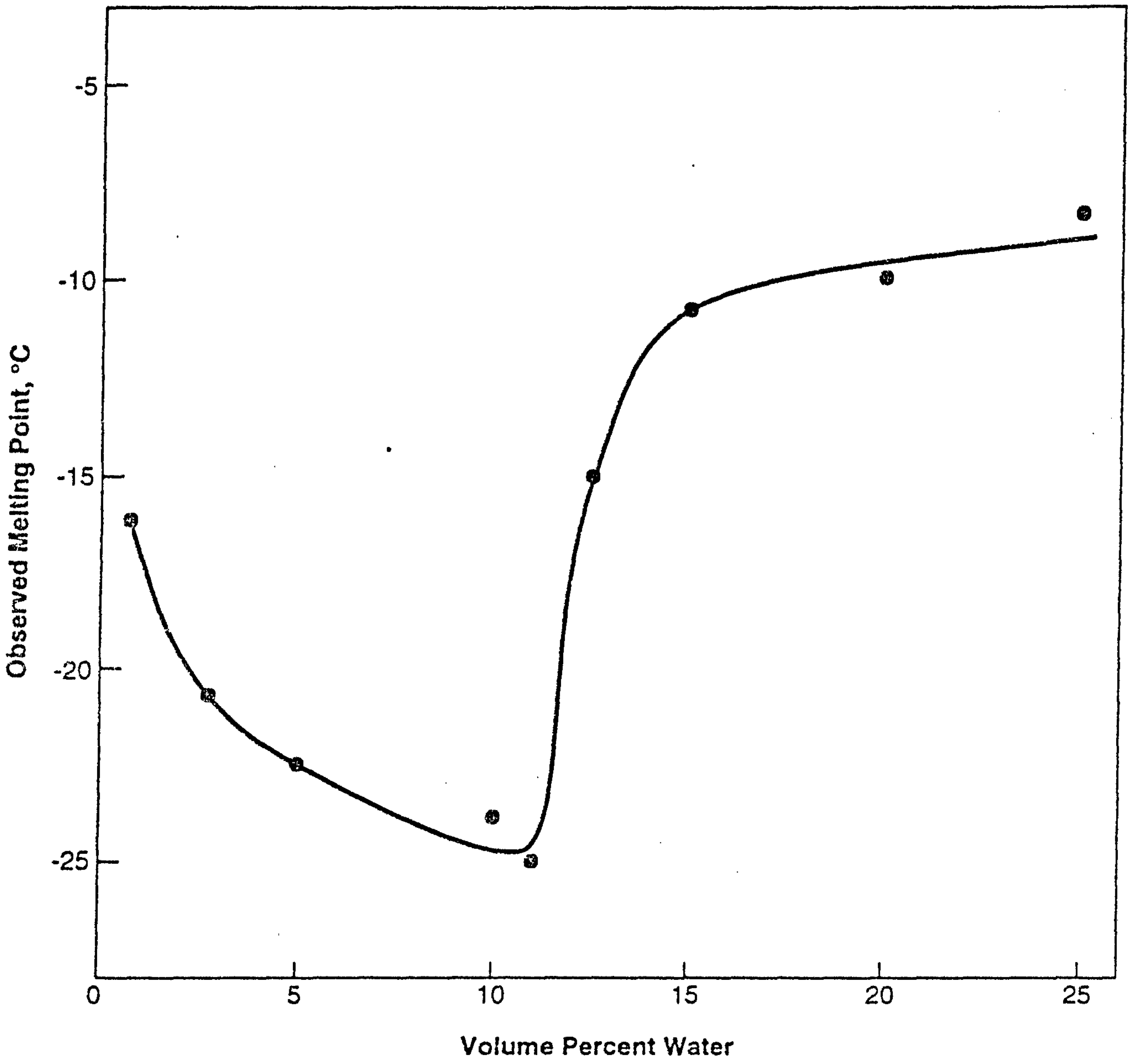


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Figure 10. Effect of water content on melting point of 60/40 3-methyl-sulfolane/sulfolane mixture.

It should be noted that this method was sufficiently sensitive to show the presence of two different melting points that occur at water concentrations above 11%. The upper melting point was recorded and used in preparing the plot presented in Figure 10.

3.4.3 Oxidative Reactivity with Thickened Simulant

The final phase of laboratory work to be performed was the development and use of a simple calorimeter to demonstrate the relative reactivities of the four DAM formulations with K-125 thickened simulant. The compositions of the four formulations were:

1. Reference Formulation

   30 vol % *N*-cyclohexyl-2-pyrrolidinone
   20 vol % water
   50 vol % of 8% by weight aqueous HTH solution

2. Minimum Freezing Point Formulation

   31 vol % "A" component consisting of
      11.0 vol % water
      35.6 vol % sulfolane
      53.4 vol % 3-methylsulfolane
   19 vol % water
   50 vol % of 8% by weight aqueous HTH solution

3. Sulfolane Formulation

   30 vol % sulfolane
   20 vol % water
   50 vol % of 8% by weight aqueous HTH solution

4. 3-Methylsulfolane Formulation

30 vol % 3-methylsulfolane
20 vol % water
50 vol % of 8% by weight aqueous HTH solution

Each of these four formulations supplies an effective 4 wt % solution of HTH that is quite stable, retaining 93% to 95% of its reactivity for 6 hr at room temperature for the sulfolane formulations and 88% for the CHP formulation.

Attempts to access the effectiveness of these formulations against a thickened agent simulant (5 wt % K-125 acrylate polymer mix in diethyl malonate) using both the dynamic mechanical analysis (DMA) spring damping method to estimate reaction mass viscosity, and the drop of agent simulant falling in the DAM formulation met with failure. The DMA spring method failed because the device was not sensitive enough to show any changes in viscosity on contact with a drop or two of the DAM formulations. A drop of the thickened simulant would float on the surface of a column of the sulfolane and 3-methylsulfolane/sulfolane formulations while it would sink into the CHP and 3-methylsulfolane formulations precluding a uniform evaluation of the formulation reactions to the thickened agent. The high density (≅ 1.2 g/cc) of sulfolane produced this behavior. The failure of the two proposed evaluation procedures forced a search for an alternative procedure. The use of differential scanning calorimetry (DSC) was examined. It was found that the reactions were very fast; by the time the microsample pan was weighed and loaded with ~ 10 mg of thickened simulant and 20 mg of the DAM formulation and was placed in the DSC cell, the reaction was nearly complete and the sample was cooling. Attempts to direct load the pan while it was in the DSC cell were too imprecise and provided only very erratic results.

Direct measurement of the temperature of the reaction mass (50 µL of thickened simulant and 100 µL of the DAM formulation) proved to be an effective method for estimating the relative reaction rates of the formulations with thickened simulant. The results obtained using the direct heat of reaction measurement technique on the four trial formulations is presented in Table 6. Six replicate determinations were made for each formulation. In only one case, the sulfolane DAM formulation, was the data so scattered that one test result set could be

Table 6. OXIDATIVE REACTIVITY TEST RESULTS

	Reaction property		
Formulation	Max ΔT, °F	React. rate index, °F/min	Seconds to Max T
3-Me DAM, n=6			
$\bar{X}$	+4.68	6.47	167
σ	0.370	0.523	15.9
C of D	7.90%	8.29%	9.52%
Sulfolane DAM, n=5+1 outlier			
$\bar{X}$	+5.62	6.36	113
σ	0.368	1.22	4.15
C of D	6.56%	19.3%	3.68%
3 Me/S DAM, n=6			
$\bar{X}$	+5.84	8.63	140
σ	0.301	0.482	10.6
C of D	5.14%	5.59%	7.61%
CHP DAM, n=6			
$\bar{X}$	+4.04	4.72	161
σ	0.680	0.888	17.2
C of D	16.2%	18.8%	10.7%

$\bar{X}$ = mean test value
σ = standard deviation
C of D = coefficient of deviation

rejected on the basis that two of the three parameters measured were more than two sigma (2 σ) different than the mean value for the six tests. This one test was declared an "outlier" and was not used in calculation of the formulation tests $\bar{x}$, σ, and C of D calculations.

In terms of the two most important test results, the maximum temperature rise (ΔT Max) and the reactive rate index (°F/min) showed that the 3-methylsulfolane/sulfolane cosolvent formulation (3 Me/S DAM) was significantly faster (nearly 2X) than the *N*-cyclohexyl-2-pyrrolidinone (CHP) formulation. The two formulations based on 3-methylsulfolane (3-Me/DAM) and sulfolane (S/DAM) reacted significantly faster than the CHP formulation. Reactivity measurements of this type should be performed in a constant temperature (±1°F) chamber.

The data obtained do indicate that all three of the trial formulations are superior to the CHP formulation in terms of relative oxidative reactivity. This test procedure should be readily adopted for use with thickened agents under "surety" laboratory conditions because relatively small (50 µL or less) samples are required.

SECTION 4

SUMMARY AND CONCLUSIONS

4.1 SUMMARY

The major areas of investigation and the principal results obtained in each area are summarized as follows.

4.1.1 Analysis and Stability of Aqueous Hypochlorite

Modification of the analytical procedures of ASTM Method D 2022(89), "Standard Test Methods of Sampling and Chemical Analysis of Chlorine Containing Bleaches," produced analytical results statistically identical with the standard method. The batch of commercial high test hypochlorite (HTH) obtained from Bio-Lab, Inc., was found to be 71.06 ± 0.648 wt % $Ca(OCl)_2$. Nominal 2 and 4 wt % solutions of this HTH were found to be equally stable for at least a 6-hr period in deionized and synthetic seawater. Statistically, no degradation (loss of active chlorine content) was found at the end of this test period.

4.1.2 Selection of Candidate Solvent Systems

The use of solubility parameters to estimate the solvent properties of organic fluids proved to be of value in selecting fluids that would dissolve the K-125 acrylate polymer thickener. The data and procedures for interpreting the importance of the three partial components (δ_d, δ_p, δ_h) described by Van Krevelen (Ref. 1) was used to calculate the solubility parameters of the K-125 polymer mix and to estimate its solubility in selected solvents. These techniques were also used to assist in selecting the structure of a candidate solvent for attempted synthesis. Solubility parameter considerations combined with structure effects or a compound's resistance to oxidation provide a rational approach to solvent selection for this demanding application.

4.1.3 Oxidative Stability of Selected Solvents

As described in Section 3, there were only four solvents in addition to the *N*-cyclohexyl-2-pyrrolidinone that had adequate resistance to oxidation in aqueous 4% HTH. The two alcohols were not suitable in terms of their low flash point (*t*-butyl alcohol) or physical state (2,5-dimethyl-2,5-hexanediol, mp = 88° to 90°C). The two sulfolanes, tetrahydrathiophene-1,1-dioxide and 3-methyltetrahydrathiophene-1,1-dioxide, were superior to all the pyrrolidinones examined. The melting points of these two solvents were too high (27° and −2°C, respectively) for consideration in light of the low temperature stability goals required for long-term field storage. Fortunately, mixtures of these two solvents with small amounts of water (≅ 10 vol %) produced a mixture with a −25°C (−13°F) melting point closely approximating the −30°C (−22°F) low temperature goal.

The oxidative stability of a mixture of these two solvents (60 vol % 3-methylsulfolane, 40 vol % sulfolane) in 4 wt % HTH aqueous solution was better than 97% retention of HTH oxidative activity for 6 hr. Thus the solvent mixture is the prime candidate for replacement of *N*-cyclohexyl-2-pyrrolidinone.

4.1.4 Low Melting Point Solvent Mixture

In order to have a field use-compatible solvent for the DAM system, the target freezing point for this component was set at −30°C (−22°F). This low melting point is required to ensure that storage containers do not require heating prior to use in making the "A" (solvent 60 vol %, water 40 vol %) component of the DAM formulation. As described in Section 3 of this report, it was possible to produce a low melting fluid mixture of the two sulfolanes and water that had a melting point of −25°C (−13°F). The composition of this mixture was 11.0 vol % water, 35.6 vol % sulfolane and 53.4 vol % 3-methylsulfolane.

4.1.5 Solubility of K-125 Polymer in the Sulfolanes

In order to produce effective decontamination of a surface covered with thickened agent droplets using a water-solvent-oxidant decontaminant, the solvent must swell and penetrate the droplet and the layer of polymeric thickener that forms at the air/droplet interface. Solubility of the polymeric thickener in the solvent(s) portion of the DAM formulation is of prime importance. Both of the sulfolanes proved to be solvents for the K-125 polymeric thickener at a 5.0 wt % concentration. Complete, stable solution of K-125 was observed with 3-methylsulfolane. This observation was somewhat surprising in light of the high solubility parameter of this compound. The total solubility parameters of sulfolane is 27.5 $\mathrm{J}^{1/2}\bullet\mathrm{cm}^{-3/2}$, that of 3-methylsulfolane is 25.46 $\mathrm{J}^{1/2}\bullet\mathrm{cm}^{-3/2}$, while the δ_T for K-125 was calculated at 19.7 $\mathrm{J}^{1/2}\bullet\mathrm{cm}^{-3/2}$. This large difference infers that the K-125 would be insoluble in these two compounds. Calculation of the $\overline{\Delta\delta}$ by Van Krevelen's method (Ref. 1) yielded values of 12.3 for 3-methylsulfolane, 15.3 for sulfolane, and 13.5 for a 60/40 solvent blend. When the $\overline{\Delta\delta}$ is 5 or less, the solvent-polymer system is considered to have good solubility. Despite these estimates, 3-methylsulfolane proved to be a "good" solvent for K-125. Sulfolane could only be considered a "near" solvent, as the solution obtained was unstable and reverted to a gel with time.

Examination of the effect of 35 vol % aqueous mixtures of both 3-methylsulfolane and sulfolane on K-125 polymer powder showed that the greatest swelling and particle agglomeration was produced by 3-methylsulfolane. Sulfolane and *N*-cyclohexyl-2-pyrrolidinone at the same concentration in water produced less swelling and very little particle agglomeration.

These observations suggest that 3-methylsulfolane would be the best DAM solvent in terms of oxidative stability and power to dissolve the polymeric thickener. However, in order to meet the low melting point requirement, it is necessary to use a mixture of 3-methylsulfolane, sulfolane, and water. Optimization of this mixture should be directed toward incorporating the maximum possible amount of the 3-methylsulfolane.

4.1.6 Reactivity of Candidate DAM Formulations

Measurement of the degree and rate of heat generation on exposure of a static 50-µL portion of thickened simulant (5 wt % K-125 in diethylmalonate) to a 100-µL portion of candidate DAM formulations in a micro test tube proved to be an effective method for comparing different formulations. This rather crude, but effective calorimeter readily demonstrated that the sulfolane formulations were at least 50% more reactive than the *N*-cyclohexyl-2-pyrrolidinone (reference) formulation. A synergism was observed with mixed sulfolane formulation when the rate of heat generation (reaction) was about 30% greater than the two single solvent sulfolane formulations and nearly twice as fast as the reference formulation.

As the 100-µL DAM formulation gently flowed (without mixing) over the exposed thickened simulant surface, this test procedure provided a measure of the DAM formulation's ability to penetrate the simulant air interface (with the thickener film being allowed 30 min to form) and to react with the simulant. This simple test thus allowed the generation of a numerical rating of formulation activity in a regime simulating field conditions. The results obtained showed, unequivocally, that the sulfolane-based formulations were at least equal to the *N*-cyclohexyl-2-pyrrolidinone formulation and perhaps as much as 50% faster. Based on the results obtained, a component "A" solvent formulation, consisting of a mixture of 3-methylsulfolane, sulfolane, and sufficient water to produce a minimum melting point, is recommended for replacing the *N*-cyclohexyl-2-pyrrolidinone formulation. The specific formulation for the "A" solvent is:

3-Methylsulfolane	53.4 parts by volume
Sulfolane	35.6 parts by volume
Deionized water	11.0 parts by volume

A 1-L quantity of this solvent mixture was prepared and shipped to ERDEC for evaluation.

4.2 CONCLUSIONS

Significant conclusions derived from this investigation, which are directly related to the sulfolane solvent system (3-methylsulfolane/sulfolane/water mixture) and the DAM formulation requirements, are presented as follows.

4.2.1 Health Hazard—Favorable

Sulfolane is only moderately toxic by subcutaneous injection with an LD_{50} value of 3.5 g/kg body weight in rabbits. LD_{50} by ingestion was 1.9 to 5.0 g/kg.

Sulfolane is a minimal and transient eye and skin irritant. Inhalation of vapors is not considered dangerous as the vapor pressure at ambient temperatures is very low (boiling point is 287°C). Inhalation of aerosols should be avoided.

The data on 3-methylsulfolane are very limited and should be established prior to field use of any DAM formulation containing this fluid. It would be expected from the similarity in structure and the similarity in physical properties that its toxicological properties will be quite like those of sulfolane.

4.2.2 Flammability—Acceptable

The flash points of these two solvents are very high; sulfolane at 165° to 178°C (329° to 352°F) and 3-methylsulfolane at 163°C (325°F). Thus these two solvents will create no significant fire hazard at ambient temperature.

4.2.3 Compatibility with Coatings—Unknown

Not considered in this investigation.

4.2.4 Mixability—Acceptable

The two solvents are completely miscible in water and are of low viscosity, ≅ 10 cP at ambient temperature. Their densities are in the 1.2 g/cm^3 range which, with their fluidity, should not lead to problems in low intensely mixing operations.

4.2.5 Decontamination Efficiency—Unknown

Determination of this property was not within the scope of this program. No testing with surety compounds could be performed.

4.2.6 Residual Effects—Favorable

As the two sulfolane solvents are completely soluble in water, very little residue will be left after the final water rinse of a decontaminated surface. The sulfolanes should be superior to the pyrrolidinones, because there is far less chance for oxidized solvent products to be formed.

4.2.7 Mixed DAM Use Temperature Range—Acceptable

The high thermal and oxidative stability of these sulfolanes suggest that temperatures as high as 60°C could be tolerated. At that temperature, the HTH thermal decomposition rate would be quite high, however.

4.2.8 Salt and Brackish Water Compatibility—Acceptable

No precipitation of other instability problems are expected. Stability in synthetic seawater was demonstrated.

4.2.9 Storage Stability—Acceptable

The thermal and oxidative stability of these two sulfolanes indicate a long stable storage life even in the presence of 11% water. Only the problems associated with storing a "wet" solvent mix need be considered in selecting storage containers.

4.2.10 Effective Pot Life—Acceptable

As demonstrated in oxidative stability tests, DAM formulations based on the binary sulfolane solvent mixture and a 4 wt % concentration of HTH, the effective pot life at ambient temperature was more than 6 hr, exceeding the 4-hr goal.

4.2.11 CAM Compatibility—Unknown

This area of compliance could not be evaluated during this program. In light of the very low ambient vapor pressure (< 0.01 Torr) of these two solvents, it is expected that any interference with CAM sensitivity would be minimal.

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SECTION 5

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APPENDIX A

LITERATURE SURVEY

A cursory examination of the literature was undertaken to ascertain potential solvent candidates. Two major classes of compounds, the *N*-substituted pyrrolidinones and sulfolanes, were searched in more detail. The *N*-substituted derivatives of a 5-member ring with two heteroatoms, i.e., 2-oxazolidinone, were briefly visited. Two primary references on solubility parameters and several additional recent publications on three-dimensional solubility parameters were reviewed.

N-Substituted Pyrrolidinones

A number of *N*-substituted pyrrolidinones were evaluated as potential solvent candidates. To broaden this material base, information on *N*-substituted pyrrolidinones not commonly available was searched for as well as their methods of preparation and their physical properties.

Technical Bulletin 2300-003R2, "*N*-Substituted Pyrrolidinones," GAF Corporation (1981).

Gaffield, W., L. W. Keefer, and P. P. Roller, "Synthesis of the Selective Bladder Carcinogen *N*-(*n*-Butyl)-*N*-(3-carboxypropyl) Nitrosamine," *Organic Preparation Proceeding International*, 9, 49-52 (1977).

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Landini, D., and F. Rolla, "A Convenient Synthesis of *N*-Alkylphalimides in a Solid-Liquid Two-Phase System in the Presence of Phase-Transfer Catalysts," *Synthesis*, 389-391 (1976).

Hort, E. V., and L. R. Anderson, "Pyrrole and Pyrrole Derivatives," Kirk-Othmer, *Encyclopedia of Chemical Technology*, 19, 499-520, 3rd ed., John Wiley, New York (1982).

Sulfolane

Sulfolane, tetrahydrothiophene-1,1-dioxane, is a colorless, highly polar, water-miscible, relatively unreactive chemical. The chemical stability and success of sulfolane in our solvent formulation evaluations dictated that we identify other potential derivatives of sulfolanes as possible candidate solvents. The following selected citations on sulfolane were evaluated to this end. The 3-methyl derivative was identified as meeting many of our solvent criteria. The literature was very limited on the 3-methyl analog; however, excerpts of an internal report from Shell International provided detailed information unavailable in the open literature. This information is appended.

Technical Information of Sulfolane Bulletin 524, Special Product Division, Chemical Department, Phillips Petroleum Company.

Technical Bulletin 1C:71-20, Sulfolane, and SC798-90 Shell Sulfolane-W, Shell Chemical Company, Industrial Chemicals Division.

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Loev, B., "Sulfolane Derivatives," *J. Amer. Chem. Soc.*, 66, 4394-4399 (1961).

Oxazolidone

The oxazolidones are a family of 5-member rings containing nitrogen and oxygen heteroatoms separated by a carbonyl functionality. They could be thought of as cyclic urethanes. They can be readily prepared by reaction of isocyanates with epoxides. A literature search was conducted by CAS numbers looking for a combination of cyclohexyl isocyanate with the common epoxides of cyclohexane oxide, ethylene oxide, propylene oxide, and styrene oxide. These would yield *N*-cyclohexyl oxazolidone for comparison to *N*-cyclohexyl pyrrolidinone. There were no references to any of these desired compounds from 1967 to present. The *N*-methyl derivative, 3-methyl-2-oxazolidinone, was commercially available from Aldrich. It was evaluated in our active chlorine test and found to be less chemically stable than the corresponding *N*-methyl pyrrolidinone. This family of compounds was therefore abandoned as potential solvent candidates.

Solubility Parameters

The basic references of Van Krevelen and Barton provided the basis for evaluating the solubility parameter of our solvent mixtures. In addition to these, several other recent studies using the three-dimensional solubility parameter concept to ascertain miscibility and solubility of polymer blends were also utilized.

Van Krevelen, D. W., *Properties of Polymers*, Elsevier, New York, pages 76-88 and pages 200-220 (1992).

Barton, A. F. M., *Handbook of Solubility Parameters and Other Cohesion Parameters*, 2nd ed., CRC Press (1991).

David, D. J., and T. F. Sincock, "Estimation of Miscibility of Polymer Blends Using the Solubility Parameter Concept," *Polymer*, Vol. 33, 4305-4514 (1992).

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APPENDIX B

INDUSTRIAL CONTACTS

Sulfolane and 3-Methylsulfolane

There are two producers of sulfolane, Phillips Petroleum Company, Bartlesville, Oklahoma, and Shell International Chemical Company, England. Shell once produced sulfolane in the United States but has recently closed its U.S. facility and now produces sulfolane only in England.

The methyl derivative, 3-methylsulfolane, was recently produced as a developmental chemical in England, but it is no longer in production. Considerable information was obtained from an internal report of Shell's, and since this information was not available in the open literature, it has been included in this report. Some of the figures and tables mentioned in the Shell text were not included, and none of the references cited were included.

If demand were appropriate, their process could be restarted with an estimated cost (9/93) of ~ $6/kg on ton quantities.

The Shell contact in England was Mr. Mike Day, overall coordinator for all of Shell Synthetic Chemicals, telephone: 71-934-5448, fax: 71-934-3558.

Phillips Petroleum Company presently supplies the 3-methylsulfolane as a developmental chemical. Their present price is ~ $20/lb as a specialty chemical. The contact at Phillips was Mr. John Roberts, telephone: 918-661-5178, fax: 918-661-8379. The 3-methylsulfolane used in our studies came from Phillips.

Pyrrolidinones

The pyrrolidinones are no longer available from the GAF Corporation. They are now available from ISP (International Specialty Products), telephone: 1-800-323-2272. ISP does not supply the dodecyl derivative anymore; they, however, do supply the *N*-cyclohexyl pyrrolidinone. The *N-tert* butyl derivative was not available, even as a specialty chemical.

typical physical properties of

SULFOLANE

Formula	$C_4H_8SO_2$
Molecular Weight	120.17
Appearance	Clear Liquid
Specific Gravity, 30/4C	1.261
100/4C	1.2012
Density, lbs/gal, 60°F	10.5
Density, g/ml, 60°F	1.276
Boiling Point, °F	545
Freezing Point, °F (99.8+ wt. % Sulfolane)	78.8
Flash Point, °F	330
Vapor Pressure, mmHg., at 302°F	14.53
320°F	21.55
392°F	85.23
410°F	115.1
500°F	421.4
Viscosity, cp. at 30°C	10.3
50°C	6.1
100°C	2.5
150°C	1.4
200°C	1.0
Refractive Index, 30°C/D	1.48
Heat of Vaporization Btu/lb. mole, at 212°F	27,000
392°F	26,500
Heat Capacity of Liquid, Btu/lb. °F, at 212°F	0.40
392°F	0.46
Heat of Fusion, Btu/lb	4.92
Dielectric Constant (30°C)	44.0
Coefficient of Thermal Expansion at 82°F per °F	3.83×10^{-4} (1)
Thermal Conductivity (2), Btu/(hr.) (Sq. Ft.) (°F/ft.)	
50	0.107 (3)
50	0.098 (4)
100	0.114
135	0.112

---

(1) This value calculated from the empirical equation $a = 0.000383 - 2.5 \times 10^{-7} (t-82)$.
where a = coefficient of expansion
t = temperature, °F in the applicable range of 32°F to 400°F. Base temperature is 82°F which is the melting point of pure sulfolane.

(2) The sulfolane used in the conductivity test contained 1.5 wt. % water as determined by freezing point and Karl Fisher water analysis.

(3) Below the freezing point.

(4) The sulfolane used in this conductivity test was the same as in Note 2 except it contained 4.5 wt. % benzene + 5.0 wt. % toluene.

Shell Chemicals

Shell International Chemical Company Limited

Facsimile message

Date: 15/10/93

To: MIDWEST RESEARCH INSTITUTE
att. Mr. T. BYERLEY
USA

Fax no: 816 - 753 - 8420

No of pages: 14
(incl cover sheet)

From: G. GAWNE

Subject: 3-METHYL SULFOLANE

Queries and return fax:
Tel: 071 934
Fax: 071 934 3558

Sorry for delay in sending what information we ha
& hope it answers some of your questions

George Gawne

Shell Centre London SE1 7NA
Tel: (071) 934 1234 Telex 919651 SHEL A G
Registered in England: No. 228931 Registered office: Shell Centre, London SE1 7NA VAT Reg. No. GB 235 763 255 (001)

The 3-methylsulfolane was commercially available, and was further purified by distillation. Its purity was greater than 99.5 %, which was determined by the same GLC analyses as are used in the determination of the purity of sulfolane.

(b) Density

We measured the liquid density of 3-methylsulfolane in a calibrated high-pressure pyknometer[8]. The results are reported in Table I.

In Fig. 1 our data and those of Vaughn[6] are compared with the values calculated by the PPP-7 program. The three sets of data show a good agreement.

(c) Viscosity

We measured the viscosity in a standard Ubbelohde viscometer. The results are as follows:

t, °C	Viscosity, cP kN.s/m^2
37.8	7.477
60.0	4.368
98.9	2.149

In Fig. 2 our experimental values are plotted together with those measured by Vaughn and the values calculated by PPP-7.

(d) Vapour pressure

We determined the vapour pressure of 3-methylsulfolane in the temperature range 160-290 °C in a static way, as described in ref. 9. The results are given in Table II together with an Antoine equation which was derived from the experimental data. In Fig. 3 the experimental data are plotted together with the calculated ones.

(e) Refractive index

The refractive index was determined in a standard Abbe refractometer. The following values were obtained:

t, °C	Refractive index
20	1.4779
30	1.4740
40	1.4708
50	1.4667
60	1.4632
70	1.4595

(f) Physical property data sheet

From the experimental data obtained we selected the vapour pressure, density and viscosity as input for the PPP-7 program. The critical properties were calculated by Lydersen's method[10].

The heat of formation and heat capacity for the ideal gas state were calculated following Benson's method as described by Chueh[11]. The calculated gas and liquid properties are given in Table III.

II-3. Vapour-liquid equilibria of the 3-methylsulfolane-water system

Since no data of the system 3-methylsulfonane-water were available, and water will almost invariably be present in the sulfolane extraction process, we determined the vapour-liquid equilibria for this system. For this purpose we adopted the P-x method, i.e. we measured the total pressure of several compositions as a function of temperature. The experimental procedure was identical with the one we used for the system sulfolane-water[3].

The data obtained are listed in Table IV. The derivation of the activity coefficients is described in the theoretical section.

II-4. Mutual solubilities of 3-methylsulfolane-hydrocarbon systems

The knowledge of the mutual solubilities of hydrocarbon-solvent systems is of essential importance in extraction calculations. Therefore we determined the mutual solubilities of 3-methylsulfolane with four n-alkanes, cyclohexane and methylcyclohexane. We could not include alkylbenzenes, since n-pentylbenzene is still completely miscible with 3-methylsulfolane. The procedure we used was the cloud-point method. In it, known amounts of 3-methylsulfolane and hydrocarbon were added in a thermostatted vessel. The temperature of the vessel was raised until the liquid was clear. Then the temperature was lowered slowly, until the first trace of a haze was observed. The temperature was measured with a thermocouple, within ± 0.05 °C.

The results are reported in Tables V and VI. In the theoretical section the calculated values are compared with the experimental data.

II-5. 3-Methylsulfolane-sulfolane systems

(a) Solid-liquid equilibria

As sulfolane has a rather high melting point it could for practical reasons (plugging of pipes) never be used as a pure solvent. This is one of the reasons why sulfolane in commercial operation always has a small water content. Therefore, if one was to use mixtures of sulfolane and 3-methylsulfolane the addition of water would no longer be necessary. To demonstrate this we measured solid-liquid equilibria in the system sulfolane-3-methylsulfolane.

The mixture of the two sulfolanes was slowly cooled down at a temperature far below the actual melting point until crystallization suddenly started, giving a sharp rise in temperature. From that moment the cooling was stopped and the sample allowed to heat up very slowly.

At the instant when the last trace of solid phase disappeared there was a sharp change in the slope of the time-versus-temperature plot. This temperature was taken as the point where the liquid phase was in equilibrium with the solid phase.

Our results are given in Table VII and plotted. From the plot it is obvious that sulfolane has a solid-phase transition point at 14.6 °C. This was also reported by Janelli[12] who measured solid-liquid equilibria in the system sulfolane-benzene, and by Della Monica[13]. Both authors give a transition point of 15.45 °C. It can also be concluded that sulfolane and 3-methylsulfolane form a 1-to-1 complex in the solid phase. In the region of approx. 60 %m 3-methyl-sulfolane there are some indications in the diagram that complexes of other compositions are formed. However, we feel that our measurements are not sufficiently accurate to draw any further conclusions.

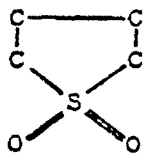
(b) Limiting activity coefficients of hydrocarbons in 3-methylsulfolane and its mixtures with sulfolane

Limiting activity coefficients of solutes in a solvent are of direct importance both for the information they give on the solvency and selectivity properties of the solvent and for the derivation of a complete description of solute-solvent systems. In earlier work[1] we already measured the limiting activity coefficients of fourteen hydrocarbons in 3-methylsulfolane and in its mixtures with sulfolane at 30, 60 and 80 °C.

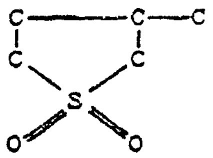
III. THEORY

III-1. General

In parts 1 and 2 of this series of reports[2,3] we first used the combination of the analytical solution of groups (ASOG) method and the non-random two-liquid (NRTL) equation for the description of liquid-vapour and liquid-liquid equilibria. The NRTL parameters are derived from limiting activity coefficients obtained by ASOG. In the ASOG method a proper count of the various groups in the molecule is required. For every hydrocarbon and for sulfolane we gave group counting rules as well as the ASOG parameters. If we want to extend our component list with 3-methylsulfolane, we may introduce a new group, but this will necessitate a considerable amount of experimental work (see refs. 2,3). A much simpler method will be to use the ASOG technique and the sulfolane-hydrocarbon parameters already available. If we look at the structure of sulfolane and 3-methylsulfolane, it will be clear that we may count 3-methylsulfolane as a number of sulfolane groups (not five as we did for sulfolane but less) and a number of CH_3 or CH_2 groups for the CH_3 group attached to the sulfolane ring. The α values for the NRTL equation for 3-methylsulfolane-hydrocarbon systems might be chosen to be the



and



same as those for the sulfolane-hydrocarbon systems.

The technique just described requires a minimum amount of experimental data and, as we will show below, produces good results. We thus derived the group counting rules for 3-methylsulfolane-hydrocarbons and the NRTL parameters for 3-methylsulfolane-water and 3-methylsulfolane-hydrocarbon systems. The results of the calculations are compared with experimental data.

III-2. 3-Methylsulfolane-water

From the experimental P-x measurements given in section II-3 the NRTL parameters were directly fitted in the same way as outlined in ref. 3. We arrived at the following parameters:

$C\ (1,2) = 630.633 - 1.84827 \times t$
$C\ (2,1) = 1637.42 + 4.03009 \times t$
$\alpha\ (1,2) = 0.390269 + 0.0020989 \times t$,

where 1 = 3-methylsulfolane
2 = water
t is in °C
$\alpha\ (2,1) = \alpha\ (1,2)$
C is in cal/mole

In Fig. 6 the calculated total pressures are compared with the experimental values. They show a good agreement.

III-3. 3-Methylsulfolane-alkanes systems

For the derivation of the ASOG group counts of 3-methylsulfolane we used the limiting activity coefficients of n-C_5-n-C_{10}, benzene, toluene and ethylbenzene in 3-methylsulfolane and the mutual solubilities of n-C_7, n-C_8 and n-C_9 with 3-methylsulfolane. These data were all measured at KSLA (see sections II-3 and II-4). We arrived at the following group counts:

The sulfolane ring = 4.485 sulfolane groups. The CH_3 attached to the sulfolane ring = 1.111 CH_2 groups.

The group counts for the alkanes as well as the α values for the NRTL equation were chosen the same as those used with the sulfolane-alkanes systems[3].

The NRTL parameters are listed in Table IX. In Figs. 7 and 8 the calculated mutual limiting activity coefficients are plotted together with the experimental values, while Figs. 9 and 10 represent

TABLE I

DENSITY OF 3-METHYLSULFOLANE

Temp., °C	Density, kg/cm^3
33.8	1181.2
44.7	1172.3
55.1	1163.5
90.1	1132.2
109.6	1114.9
152.0	1076.7

TABLE II

VAPOUR PRESSURE OF 3-METHYLSULFOLANE

T, °C	$P_{exp.}$ mbar	$P_{calc.}$ mbar
287.5	1014.0	1016.3
283.6	940.6	936.3
279.8	864.9	863.2
277.0	810.7	812.4
272.8	742.1	740.6
268.9	678.1	678.7
264.5	612.7	613.9
259.5	546.5	546.4
254.1	480.2	480.5
248.1	414.0	415.0
240.9	346.8	346.1
233.0	281.0	281.7
222.9	213.4	214.0
209.5	146.4	145.5
190.7	80.8	80.9
179.2	54.8	54.9
171.2	41.5	41.3
163.0	30.3	30.4

Boiling point is 287.4 °C.

$\ln P_{mbar} = 16.9343-4801.84/(192.188+t°C)$

TABLE III

```
NAME   3 MET. SULFOLANE
                                                   C5H10SO2

MOLECULAR WEIGHT (G/MOLE)
BOILING POINT (DEG C)                       134.18     (ABSOLUTE ERROR)
FREEZING POINT (DEG C)                      287.40      (       .1    )
CRITICAL TEMPERATURE (DEG C)                 -1.20      (       .07   )
CRITICAL PRESSURE (ATMOSPHERES)             561.2       (       .4    )
CRITICAL VOLUME (CC/G)                       41.8       (       .4    )
HEAT OF VAPORIZATION (CAL/G)                  2.55      (     2.      )
HEAT OF FUSION (CAL/G)                       95.16      (       .07   )
ENTHALPY OF FORMATION (CAL/G)                           (             )
FREE ENERGY, FORMATION (CAL/G)                          (             )
ENTHALPY OF COMBUSTION (CAL/G)                          (             )
FREE ENERGY, COMBUSTION (CAL/G)                         (             )
FLASH POINT (DEG C)                                     (             )
AUTO-IGNITION TEMP. (DEG C)                             (             )
EXPLOSIVE LIMITS (PERCENT VOLUME)                       (             )
      LOWER
      UPPER                                             (             )
SOLUBILITY IN WATER (  WEIGHT)                          (             )
                                                        (             )
```

GAS PROPERTIES

TEMP. DEG C	COMPRESSIBILITY FACTOR		VISCOSITY CENTIPOISES			THERMAL CONDUCTIVITY CAL/CM/SEC/DEG C (X1000)			HEAT CAPACITY CAL/G/DEG C			HEAT CONTENT CAL/G			ENTROPY CAL/G/DEG C		
	34.0	68.0	0.0	34.0	68.0	0.0	34.0	68.0	0.0	34.0	68.0	0.0	34.0	68.0	1.0	34.0	68.0
-100			.0033			.0068			.16			1097.			9.932		
-50			.0043			.010			.19			1105.			9.974		
0			.0052			.015			.223			1115.8			10.016		
50			.0060			.020			.259			1127.8			10.056		
100			.0069			.025			.295			1141.6			10.095		
150			.0076			.032			.330			1157.2			10.135		
200			.0084			.038			.364			1174.5			10.173		
250			.0091			.045			.395			1193.4			10.212		
300			.0097			.051			.423			1213.8			10.249		
350			.0104			.058			.448			1235.6			10.285		
400			.0112			.064			.470			1258.5			10.320		
450			.0116			.070			.488			1282.4			10.354		
500			.0122			.076			.504			1307.2			10.388		
550	.580		.0128	.016		.082	.13		.518	.696		1332.7	1313.6		10.420	10.345	
600	.700	.320	.0133	.015	.034	.087	.10	.19	.532	.609	.80	1338.9	1343.4	1309.	10.450	10.384	10.34

TABLE III cont'd

NAME 3 MET. SULFOLANE

LIQUID PROPERTIES AT SATURATION PRESSURE

TEMP. DEG C	DENSITY G/CC	VISCOSITY CENTIPOISES	THERMAL CONDUCTIVITY CAL/CM/SEC/C (X1000)	HEAT CAPACITY CAL/G/DEG C	HEAT CONTENT CAL/G	HEAT OF VAPORIZATION CAL/G	ENTROPY CAL/G/DEG C	ENTROPY OF VAPORIZATION CAL/G/DEG C	VAPOR PRESSURE ATM	SURFACE TENSION DYNES/CM
0	1.210	21.5	.60	.366	987.0	129.	9.754	.4712		64.
20	1.193	11.4	.57	.356	994.0	126.	9.780	.4312		61.
40	1.176	7.28	.54	.367	1001.	124.	9.806	.3962		58.
60	1.159	4.49	.51	.379	1009.	122.	9.830	.3652		56.
80	1.141	3.22	.49	.392	1016.	119.	9.853	.3382		53.
100	1.123	2.12	.47	.405	1024.	117.	9.876	.3142	.0017	50.
120	1.106	1.54	.45	.419	1033.	115.	9.898	.2922	.0048	48.
140	1.088	1.15	.43	.433	1041.	113.	9.920	.2732	.01192	45.
160	1.069	.892	.42	.447	1050.	112.	9.942	.2552	.02682	42.
180	1.052	.706	.40	.462	1059.	108.	9.962	.2392	.05562	40.
200	1.032	.569	.39	.475	1068.	106.	9.982	.2242	.1074	37.
220	1.013	.467	.37	.488	1078.	104.	10.00	.2102	.1966	35.
240	.9932	.389	.36	.502	1088.	101.	10.02	.1972	.3337	32.
260	.9734	.328	.34	.513	1098.	98.9	10.04	.1852	.5455	30.
280	.9532	.279	.33	.525	1108.	96.3	10.06	.1742	.8550	27.
300	.9324	.240	.31	.536	1119.	93.6	10.08	.1632	1.292	25.
320	.9112	.22	.30	.547	1130.	90.8	10.12	.1532	1.889	23.
340	.8893	.18	.29	.557	1142.	87.9	10.12	.1432	2.685	20.
360	.8668	.16	.27	.568	1152.	84.7	10.13	.1342	3.721	18.
380	.8435	.14	.26	.578	1163.	81.4	10.15	.1242	5.044	16.
400	.8192	.12	.25	.589	1175.	77.9	10.17	.1152	6.704	14.
420	.7938	.12	.24	.602	1187.	74.0	10.19	.1072	8.759	12.
440	.7668	.097	.22	.614	1199.	69.9	10.20	.098	11.27	9.8
460	.7382	.085	.21	.630	1212.	[illegible]	10.22	.089	14.31	7.9
480	.7067	.075		.649	1225.	60.0	10.24	.079	17.97	6.0
500	.6716	.065		.677	1238.	53.9	10.26	.069	22.34	4.3
520	.630	.056			1250.	46.	10.3	.058	27.6	2.6
540	.577	.046			1270.	36.	10.3	.044	33.8	1.2
560	.460	.032				12.	10.3	.014	41.3	.032

HEAT CONTENT REFERENCE STATE: 2000 BTU/LB (1111. CAL/G) FOR THE IDEAL GAS AT 0 DEG F (-17.78 DEG C).
ENTROPY REFERENCE STATE: 10 E.U. FOR THE IDEAL GAS AT 1 ATM AND 0 DEG F (-17.78 DEG C).

TABLE IV

TOTAL-PRESSURE MEASUREMENTS OF THE SYSTEM 3-METHYLSULFOLANE-WATER

mole fraction 3-methylsulfolane											
0.0037		0.0322		0.1460		0.6662		0.8661		0.9480	
t, °C	P_{mbar}	t, °C	P_{mbar}	t, °C	P_{mbar}	t, °C	P_{mbar}	t, °C	P_{mbar}	t, °C	P_{mbar}
26.10	32.7	23.50	28.7	26.35	32.7	20.06	20.4	30.71	25.5	25.35	6.8
35.00	51.7	38.10	63.7	36.80	65.2	40.06	58.1	49.82	59.7	41.26	19.2
45.16	90.0	48.35	108.8	45.68	95.7	56.21	124.4	70.04	124.8	60.18	42.8
53.60	146.4	55.87	158.3	55.74	155.3	70.42	222.2	87.00	216.8	73.04	68.7
60.49	201.4	66.30	259.7	62.19	229.6	80.05	320.1	101.89	337.3	82.13	90.7
72.32	339.0	73.51	355.2	72.51	329.3	90.07	460.2			91.78	121.5
79.00	451.0	80.27	483.2	79.68	442.0	97.17	587.6	125.32	635.4	100.15	154.5
86.16	598.3	88.83	654.9	88.32	627.7	101.96	681.3	135.21	808.6	110.02	203.6
92.90	774.9	94.32	807.7	93.37	759.8	110.98	908.6			119.49	258.5
99.30	983.5	99.82	985.0	99.59	948.5					130.67	340.8
				105.25	1035.8						

TABLE V

SOLUBILITY OF HYDROCARBONS IN 3-METHYLSULFOLANE

Cyclohexane		Methyl-cyclohexane		n-Hepta		n-Octane		n-Nonane		n-Decane	
t, °C	X mole percent	t, °C	X mole percent	t, °C	X mole percent	t, °C	X mole percent	t, °C	X mole percent	t, °C	X mole percent
21.8	9.28	32.4	6.25	20.8	2.88	32.0	2.23	27.7	1.40		
34.4	9.95	37.8	6.98			46.0	2.61	35.8	1.71	62.4	2.01
36.3	11.28	48.6	8.61	35.6	3.64	49.6	3.03	43.1	2.02	73.6	2.55
44.0	11.95	58.4	10.24	45.6	3.85	50.9	3.00	47.3	2.23	98.0	4.01
45.9	13.35	66.0	11.73	46.3	4.45	56.2	3.35	55.9	2.65		
50.9	14.75			60.6	5.49	58.1	3.48	56.7	2.70		
52.8	13.79			63.2	5.42	59.5	3.72	65.7	3.14		
61.8	15.90			69.9	6.29	61.2	3.69	72.8	3.57		
62.9	17.47			75.4	6.59	67.4	4.10	81.5	4.10		
68.3	17.77			79.9	7.32	70.5	4.38	86.5	4.49		
76.5	20.93					70.5	4.68				
81.6	22.66					72.3	4.64				
84.3	23.32					76.6	4.98				
						81.8	5.44				

TABLE VI

SOLUBILITY OF 3-METHYLSULFOLANE IN HYDROCARBONS

Cyclohexane		n-Heptane		n-Octane		n-Nonane	
t, °C	mole percent	t, °C	mole percent	t, °C	mole percent	t, °C	mole percent
16.1	0.41	22.2	0.43			21.8	0.62
30.5	0.70	32.6	0.61	36.4	0.74	43.0	1.12
35.6	0.84	35.9	0.63	52.0	1.10	55.3	1.42
40.2	0.98	44.0	0.81	55.3	1.23	66.5	1.73
44.5	1.12	50.0	0.96	66.6	1.62	71.2	1.94
48.7	1.28	60.2	1.26	72.3	1.90	77.4	2.28
51.5	1.40	68.1	1.54	78.2	2.26	81.8	2.56
54.2	1.54	73.7	1.80	86.0	2.68		
59.7	1.81	77.0	1.93				
64.7	2.10	79.9	2.06				
68.6	2.36	82.2	2.17				
72.5	2.66	82.9	2.24				
77.1							
80.1							
85.6							

TABLE VII

SOLID-LIQUID EQUILIBRIA IN THE SYSTEM SULFOLANE-3-METHYLSULFOLANE

Mole fraction 3-methyl-sulfolane	Temperature, °C	Mole fraction 3-methyl-sulfolane	Temperature, °C
1.0000	- 1.2	0.4695	-15.8
0.8947	- 5.3	0.4338	-17.0
0.7874	- 9.7	0.4227	-17.7
0.7063	-12.6	0.4167	-17.1
0.6786	-13.7	0.4137	-16.9
0.6670	-14.5	0.2862	- 5.2
0.6586	-15.7	0.1776	3.9
0.6461	-15.2	0.0919	10.9
0.6241	-14.9	0.0661	12.7
0.6123	-15.0	0.0462	14.0
0.5987	-15.5	0.0376	16.6
0.5815	-15.2	0.0284	19.9
0.5792	-14.9	0.0200	22.5
0.5761	-14.9	0.0164	23.4
0.5607	-15.1	0 0120	24.6
0.5423	-15.1	0.0082	25.8
0.5202	-15.3	0.0048	26.0
0.4948	-15.3	0.0000	26.2

AMGR.0118.76

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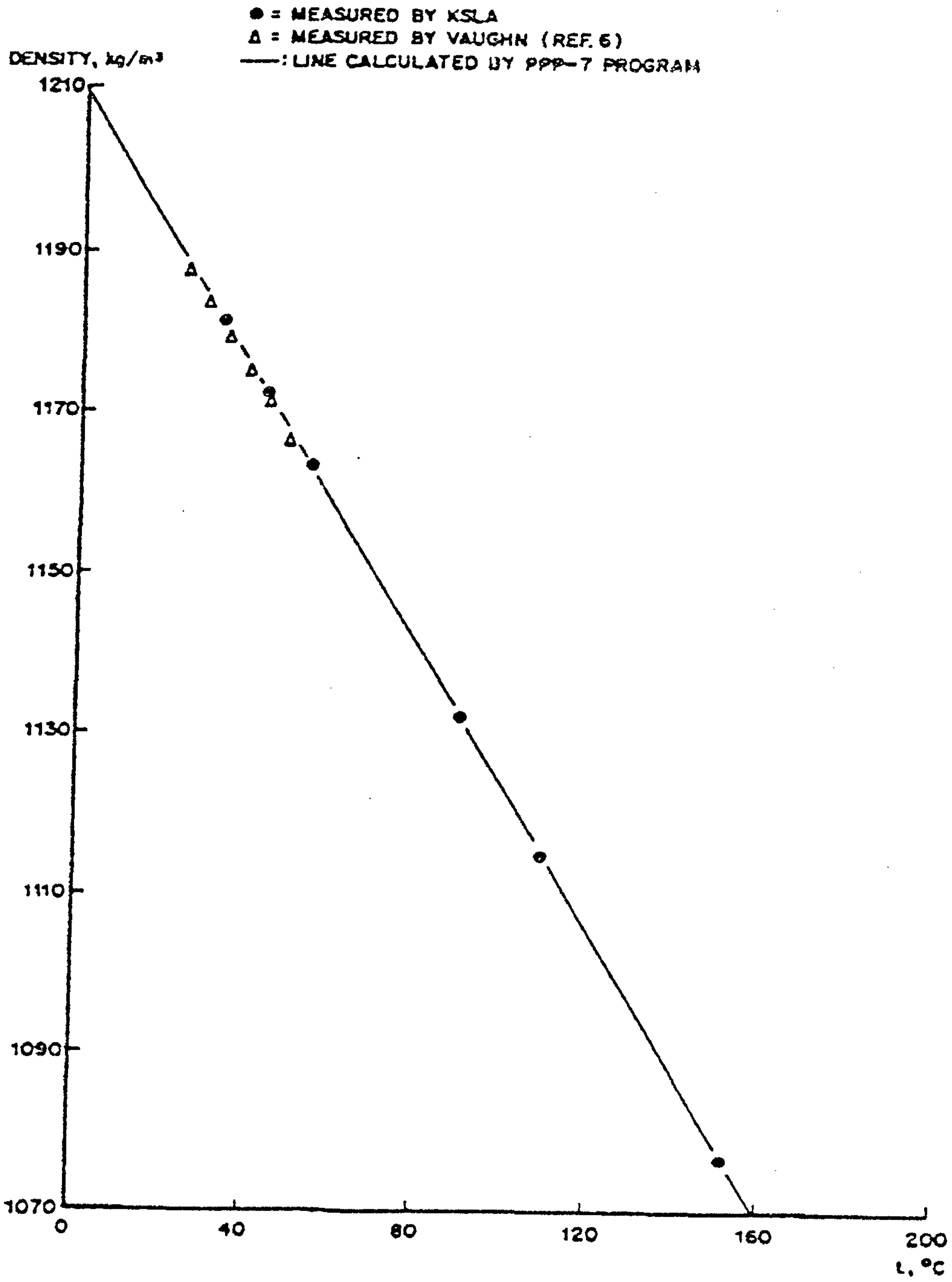
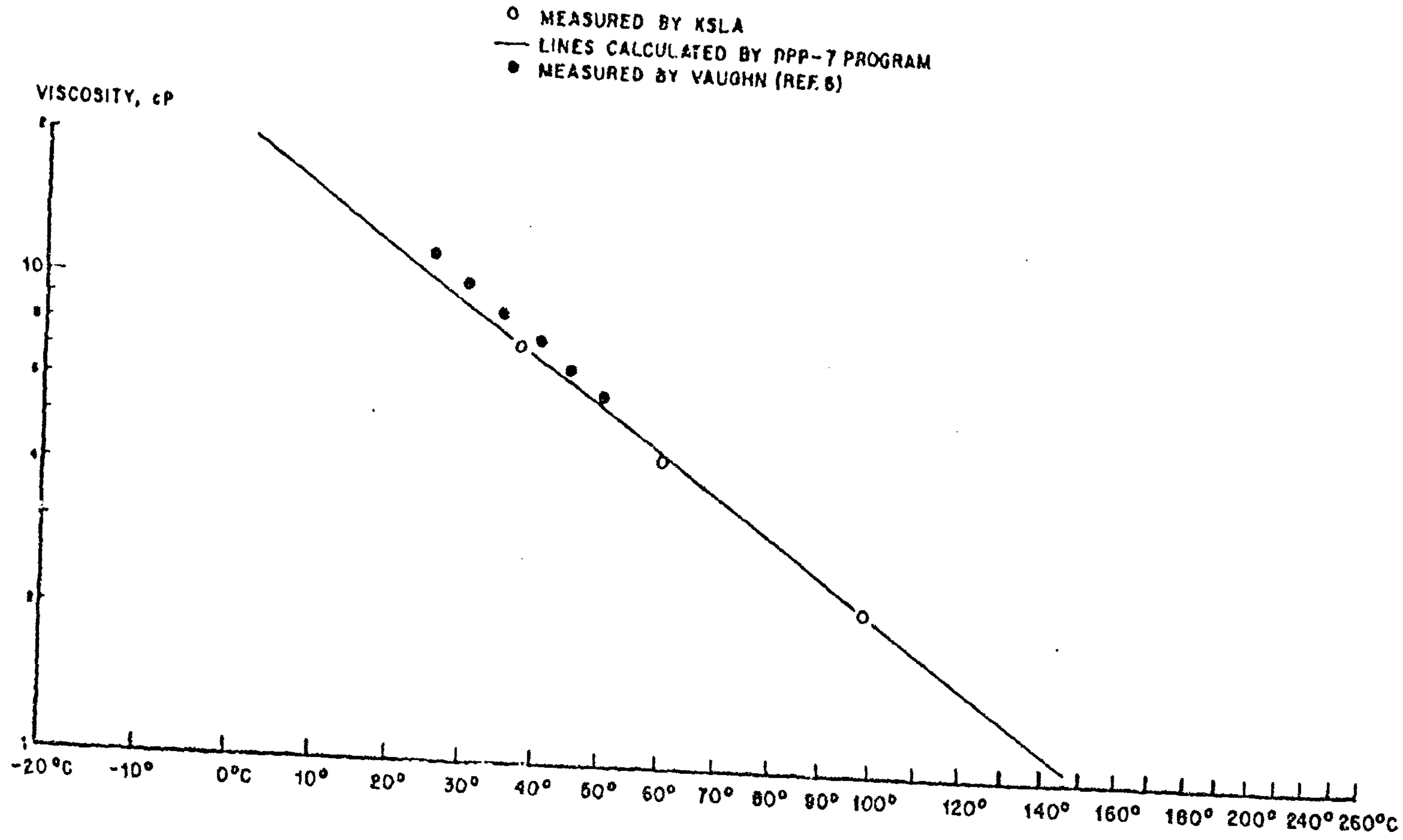


DENSITY OF 3-METHYLSULFOLANE

DRAWN NIJ
DWG 76.09.1043

AWN NIJ
DWG 76.09.1044

AMGR.0118.7



VISCOSITY OF 3-METHYLSULFOLANE

FIGUR

FIGUR

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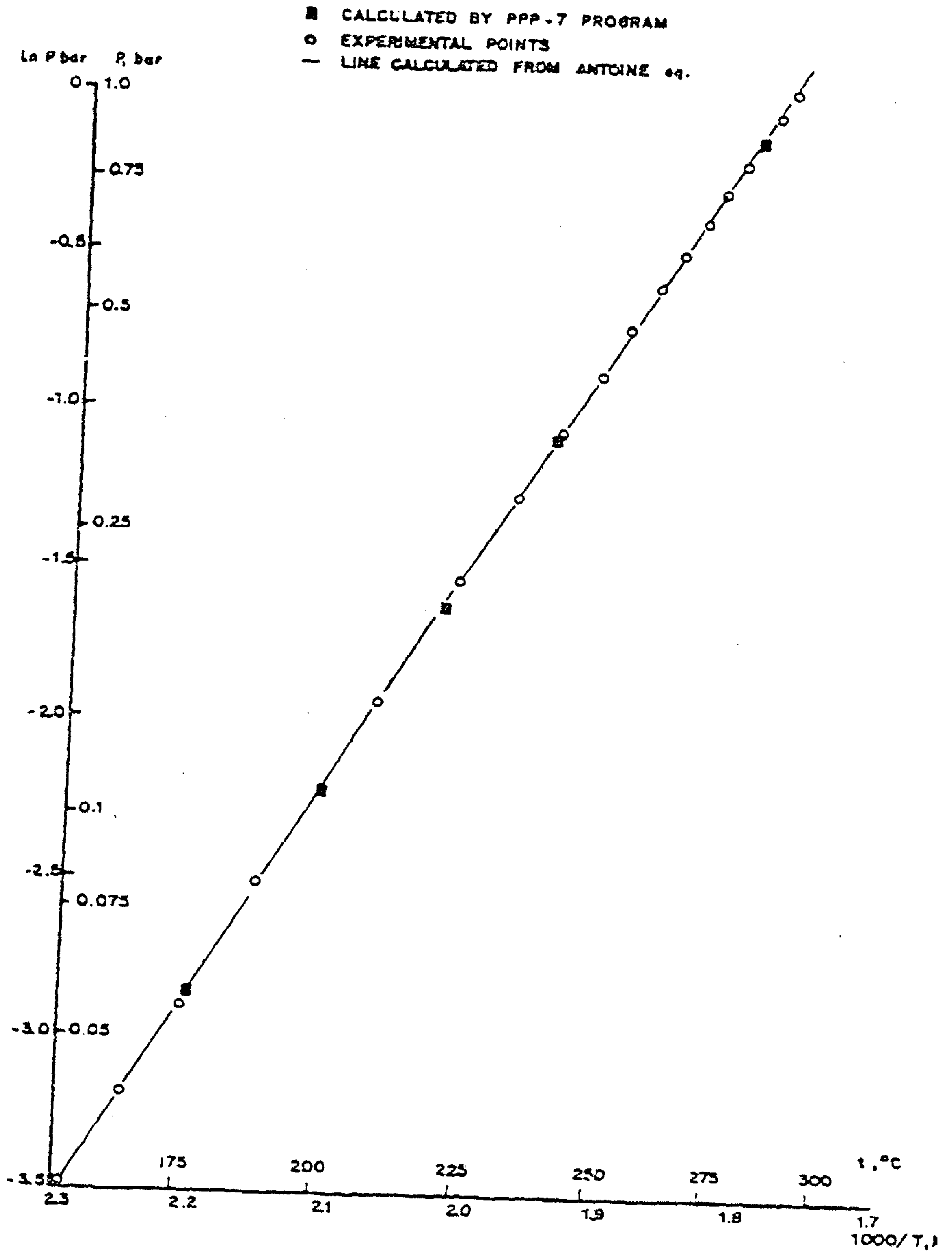

VAPOUR PRESSURE OF 3-METHYLSULFOLANE

B-17

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DWG 76.09.1045

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APPENDIX C

OXIDATIVE STABILITY TEST RESULTS

Table C-1. OXIDATIVE STABILITY TEST RESULTS: REMAINING ACTIVE CHLORINE RELATIVE TO WATER CONTROL

WATER CONTROL	TIME (hr)	REMAINING ACTIVE CHLORINE IN HTH RELATIVE TO WATER CONTROL AT 0 HR	0.5	2	4	6	
H2O	WATER CONTROL	100.0%			100.1%		
PYRROLIDINONES, SOLUBLE							
2 P	2 PYRROLIDINONE	86.2%	67.3%	25.9%	0.0%		
PNVP	POLY N-VINYLPYRROLIDONE K-30	82.4%	58.1%	23.2%	16.3%	11.5%	
NMP	1-METHYL-2-PYRROLIDINONE	70.2%	50.9%	46.4%	43.4%	45.0%	NMP/DI COOLED TO 23C
CHP	1-CYCLOHEXYL-2 PYRROLIDINONE	94.5%	91.9%	89.0%	86.6%	83.7%	MODIFIED D2022
2 HE-2-P	1-HYROXYETHYL-2-PYRROLIDINONE	65.6%	8.9%	7.6%	0.0%		
PYRROLIDINONES, PARTIALLY SOLUBLE							
NOP	1-OCTYL-2-PYRROLIDINONE	91.1%	71.6%	54.2%	27.1%	5.5%	25% DMHD IN NOP, 2% HTH – 2 PHASES
DDP	1-DODECYL-2-PYRROLIDINONE	81.3%	52.4%	20.7%	0.9%	0.0%	25% DMHD IN DDP, 2% HTH – 2 PHASES
PIPERIDONES							
VAL	VALAROLACTAM	88.3%	54.6%	37.5%	27.5%	22.0%	
MPIPER	1-METHYL-2-PIPERIDONE	92.7%	88.9%	74.2%	59.5%	42.4%	
TERTIARY ALCOHOLS							
TAML	T AMYL ALCOHOL	90.1%	107.2%	107.3%			2 PHASES
TBUOH	T-BUTANOL	101.2%	100.1%	101.2%	100.4%		
DMHD	2,5-DIMETHYL-2,5 HEXANEDIOL	89.9%	83.9%	85.2%	85.0%		10% DMHD PREDISSOLVED
DIGLYMES							
2 MEE	2-METHOXYETHYL ETHER	98.7%	96.8%	19.6%	0.0%		
2 EEE	2 ETHOXYETHYL ETHER	92.5%	77.5%	58.4%	0.0%		
DEGDBE	DIETHYLENE GLYCOL DIBUTYL ETHER	ND	ND	ND	ND	ND	2 PHASES
SUCCINIMIDES							
SUCC	SUCCINIMIDE	25.4%	36.2%	35.6%			SUCC PREDISSOLVED, IMMED RXN
NMSUCC	N-METHYL SUCCINIMIDE	105.5%	99.4%	60.1%	40.5%	32.6%	
OTHER SOLVENTS AND ADDITIVES							
PDX	p DIOXANE	92.4%	1.3%				
TX100	TRITON X 100	54.2%	59.1%	57.3%			MODIFIED D2022
TMU	1133 TETRAMETHYLUREA	89.5%	23.8%	20.3%			
TMU	1133-TETRAMETHYLUREA	101.2%	57.1%	17.6%			FRESH TMU FROM ALDRICH
MIXTURES							
5C MIX	8TX100, 10NMP, 10GBL, 10DDP	77.4%	31.6%	3.6%			
SULFONES							
SULFLNE	SULFOLANE	97.5%	96.4%	95.8%	94.9%	94.6%	
MSULFLNE	3 METHYLSULFOLANE	94.8%	94.2%	94.2%	93.5%	92.9%	
LACTONES							
GBL	γ BUTYROLACTONE	96.0%	71.0%	9.1%			CLEAR SOLUTION AT 1HR
MOXAZO	3 METHYL-2-OXAZOLIDINONE	95.3%	94.4%	73.6%	19.6%	16.0%	

Table C-2. OXIDATIVE STABILITY TEST RESULTS: DATA SORTED ACCORDING TO FUNCTIONALITY

DATA SORTED ACCORDING TO FUNCTIONALITY

ABREV	NAME	TIME (hr)	PERCENT ACTIVE CHLORINE FROM HTH 0	0.5	2	4	6	COMMENTS
WATER CONTROL								
H2O	WATER CONTROL		69.4			69.5		
PYRROLIDINONES								
2-P	2-PYRROLIDINONE		59.8	46.7	18.0			
2-P	2-PYRROLIDINONE		56.8	63.2	60.0	47.7	37.3	50% tBuOH, 2% HTH, 5% 2-P
NMP	1-METHYL-2-PYRROLIDINONE		48.1	31.8	32.8	32.2	32.1	
NMP	1-METHYL-2-PYRROLIDINONE		48.7	35.3	32.2	30.1	31.2	NMP/DI COOLED TO 23C
NMP	1-METHYL-2-PYRROLIDINONE		55.5	46.8	33.0	32.6		NMP/DI COOLED TO 5C
2-HE-2-P	1-HYROXYETHYL-2-PYRROLIDINONE		45.5	6.2	5.3			
PNVP	N-VINYLPYRROLIDONE K-30		57.2	40.3	16.1	11.3	8	
NOP	1-OCTYL-2-PYRROLIDINONE		62.3		60.2			25% DMHD IN DI + 15% NOP, 2% HTH = 2 PHASES
NOP	1-OCTYL-2-PYRROLIDINONE		60.2		58.9			25% DMHD IN DI + 15% NOP, 4% HTH = 2PHASES
NOP	1-OCTYL-2-PYRROLIDINONE		60.2	58.2	57.5			2 PHASES
NOP	1-OCTYL-2-PYRROLIDINONE		61.8	57.1	51.1		41.7	25% DMHD IN NOP, 4% HTH = 2 PHASES
NOP	1-OCTYL-2-PYRROLIDINONE		63.2	49.7	37.6	18.8	3.8	25% DMHD IN NOP, 2% HTH = 2 PHASES
NOP	1-OCTYL-2-PYRROLIDINONE		61.8	46.2	31.7			25% DMHD IN NOP, 2% HTH = 2 PHASES
DDP	1-DODECYL-2-PYRROLIDINONE		61.1	60.4	64.5			2 PHASES
DDP	1-DODECYL-2-PYRROLIDINONE		59.6	56.9	57.8			25% tBuOH, 2 PHASES
DDP	1-DODECYL-2-PYRROLIDINONE		58.2	67.6	68.0	66.9		50% tBuOH, 2% HTH, 5% DDP
DDP	1-DODECYL-2-PYRROLIDINONE		56.4	36.4	14.4	0.6		25% DMHD IN DDP, 2% HTH = 2 PHASES
CHP	1-CYCLOHEXYL-2-PYRROLIDINONE		ND	NO CL END POINT				
CHP	1-CYCLOHEXYL-2-PYRROLIDINONE		65.6	61.8	61.8	60.1	58.1	MODIFIED D2022
CHP	1-CYCLOHEXYL-2-PYRROLIDINONE		54.6	53.8	49.8			MODIFIED D2022
PIPERIDONES								
VAL	VALAROLACTAM		61.3	37.9	26.0	19.1	15.3	
MPIPER	1-METHYL-2-PIPERIDONE		64.3	61.7	51.5	41.3	29.4	
TERTIARY ALCOHOLS								
TAML	t-AMYL ALCOHOL		63.5	74.4	74.5			2 PHASES
TBUOH	T-BUTANOL		70.2	69.5	70.2	69.7		
DMHD	2,5 DIMETHYL-2,5-HEXANEDIOL		85.3	79.9	78.9			DMHD NOT SOLUBLE
DMHD	2,5 DIMETHYL-2,5-HEXANEDIOL		62.4	58.2	59.1	59.0		10% DMHD PREDISSOLVED
DIGLYMES								
2-MEE	2-METHOXYETHYL ETHER		68.5	67.2	13.6	0.0		
2-EEE	2-ETHOXYETHYL ETHER		64.2	53.8	40.5			
DEGDBE	DIETHYLENE GLYCOL DIBUTYL ETHER	2 PHASES						
SUCCINIMIDES								
SUCC	SUCCINIMIDE		65.7	58.8	46.0	42.5	39.8	SUCC NOT ALL SOLUBLE
SUCC	SUCCINIMIDE		17.6	25.1	24.7			SUCC PREDISSOLVED, IMMED RXN
NMSUCC	N-METHYL SUCCINIMIDE		73.2	69.0	41.7	28.1	22.6	
OTHER SOLVENTS AND ADDITIVES								
PDX	p-DIOXANE		64.1	0.9				
TX100	TRITON X-100		37.6	41.0	39.8			MODIFIED D2022
TMU	1133-TETRAMETHYLUREA		62.1	16.5	14.1			
TMU	1133-TETRAMETHYLUREA		70.2	39.6	12.2			FRESH TMU FROM ALDRICH
MIXTURES								
SC MIX	8TX100, 10NMP, [illegible]GBL, 10DDP		53.7	21.9	2.5			
SULFONES								
SULFLNE	SULFOLANE		67.7	66.9	66.5	65.9	65.7	
MSULFLNE	3-METHYLSULFOLANE		65.8	65.4	65.4	64.9	64.5	

Table C-3. OXIDATIVE STABILITY TEST RESULTS: DATA SORTED ACCORDING TO FUNCTIONALITY AND ONE BEST RESULT SELECTED

DATA SORTED ACCORDING TO FUNCTIONALITY, THEN PARED TO ONE BEST RESULT

ABREV	NAME	TIME (hr)	PERCENT ACTIVE CHLORINE IN HTH					COMMENTS
			0	0.5	2	4	6	
WATER CONTROL								
H2O	WATER CONTROL		69.4			69.5		
PYRROLIDINONES								
2-P	2-PYRROLIDINONE		59.8	46.7	18.0			
NVP	N-VINYLPYRROLIDONE K-30		57.2	40.3	16.1	11.3	8	
NMP	1-METHYL-2-PYRROLIDINONE		48.7	35.3	32.2	30.1	31.2	NMP/DI COOLED TO 23C
2-HE-2-P	1-HYROXYETHYL-2-PYRROLIDINONE		45.5	6.2	5.3			
NOP	1-OCTYL-2-PYRROLIDINONE		63.2	49.7	37.0	18.8	3.8	25% DMHD IN NOP, 2% HTH - 2 PHASES
DDP	1-DODECYL-2-PYRROLIDINONE		56.4	36.4	14.4	0.6		25% DMHD IN DDP, 2% HTH - 2 PHASES
CHP	1-CYCLOHEXYL-2-PYRROLIDINONE		65.6	65.8	61.8	60.1	58.1	MODIFIED D2022
PIPERIDONES								
VAL	VALAROLACTAM		61.3	37.9	26.0	19.1	15.3	
MPIPER	1-METHYL-2-PIPERIDONE		64.3	61.7	51.5	41.3	29.4	
TERTIARY ALCOHOLS								
TAML	t-AMYL ALCOHOL		62.5	74.4	74.5			2 PHASES
TBUOH	T BUTANOL		70.2	69.5	70.2	69.7		
DMHD	2,5-DIMETHYL-2,5-HEXANEDIOL		62.4	58.2	59.1	59.0		10% DMHD PREDISSOLVED
DIGLYMES								
2-MEE	2-METHOXYETHYL ETHER		68.5	67.2	13.6	0.0		
2-EEE	2-ETHOXYETHYL ETHER		64.2	53.8	40.5			
DEGDBE	DIETHYLENE GLYCOL DIBUTYL ETHER		ND	ND	ND	ND	ND	2 PHASES
SUCCINIMIDE								
SUCC	SUCCINIMIDE		17.6	25.1	24.7			
NMSUCC	N-METHYL SUCCINIMIDE		73.2	69.0	41.7	28.1	22.6	SUCC PREDISSOLVED, IMMED RXN
OTHER SOLVENTS AND ADDITIVES								
PDX	p DIOXANE		64.1	0.9				
TX100	TRITON X-100		37.6	41.0	39.8			
TMU	1133-TETRAMETHYLUREA		62.1	16.5	14.1			MODIFIED D2022
TMU	1133-TETRAMETHYLUREA		70.2	39.5	12.2			FRESH TMU FROM ALDRICH
MIXTURES								
SC MIX	8TX100, 10NMP, 10GBL, 10DDP		53.7	21.9	2.5			
SULFONES								
SULFLNE	SULFOLANE		67.7	66.9	66.5	65.9	65.7	
MSULFLNE	3 METHYLSULFOLANE		65.8	65.4	65.4	64.9	64.5	
LACTONES								
GBL	γ BUTYROLACTONE		66.6	49.3	6.3			
MOXAZO	3 METHYL-2 OXAZOLIDINONE		66.0	65.5	51.1	13.6	11.1	CLEAR SOLUTION AT 1HR

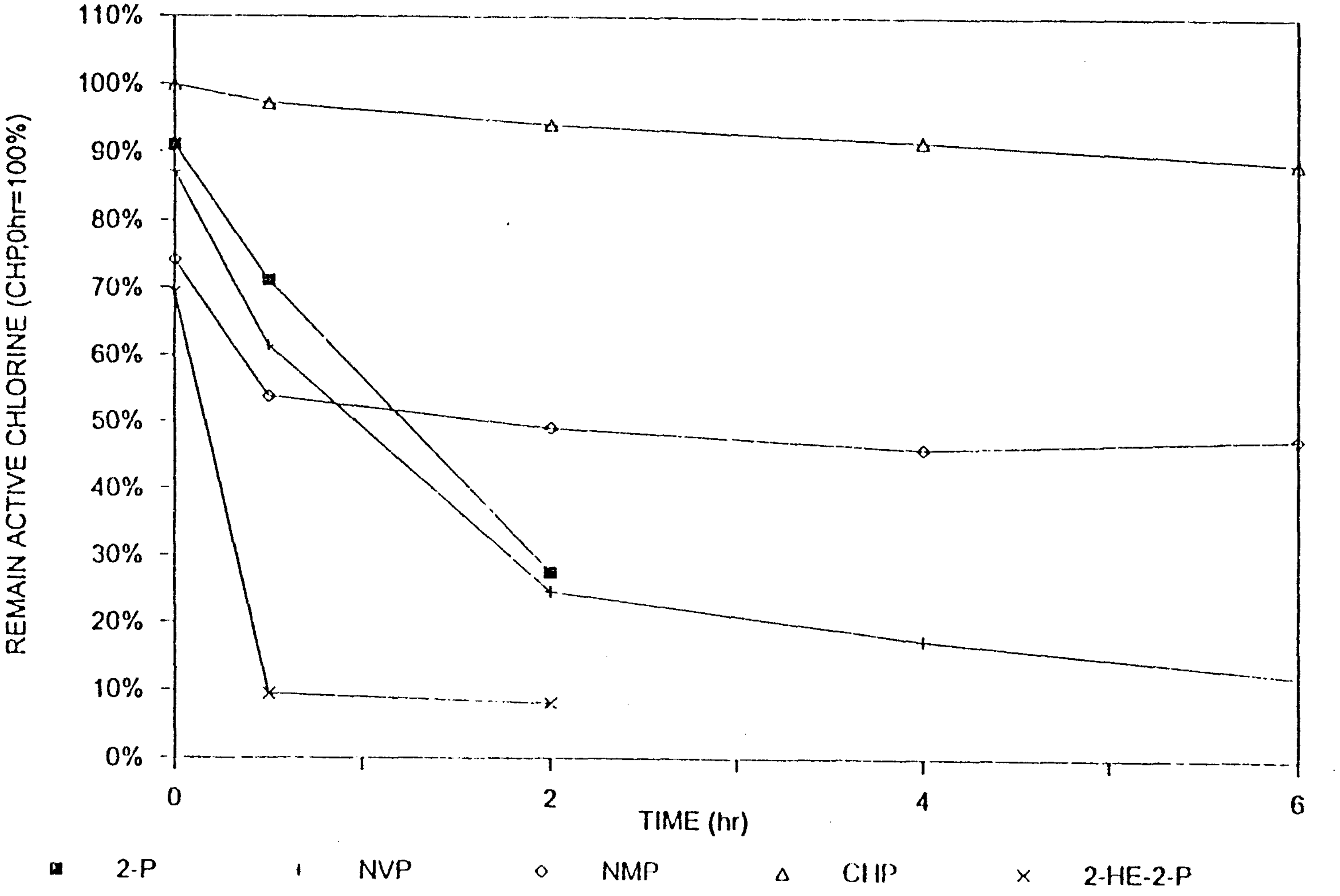

Figure C-1. Oxidative stability of soluble pyrrolidinones.

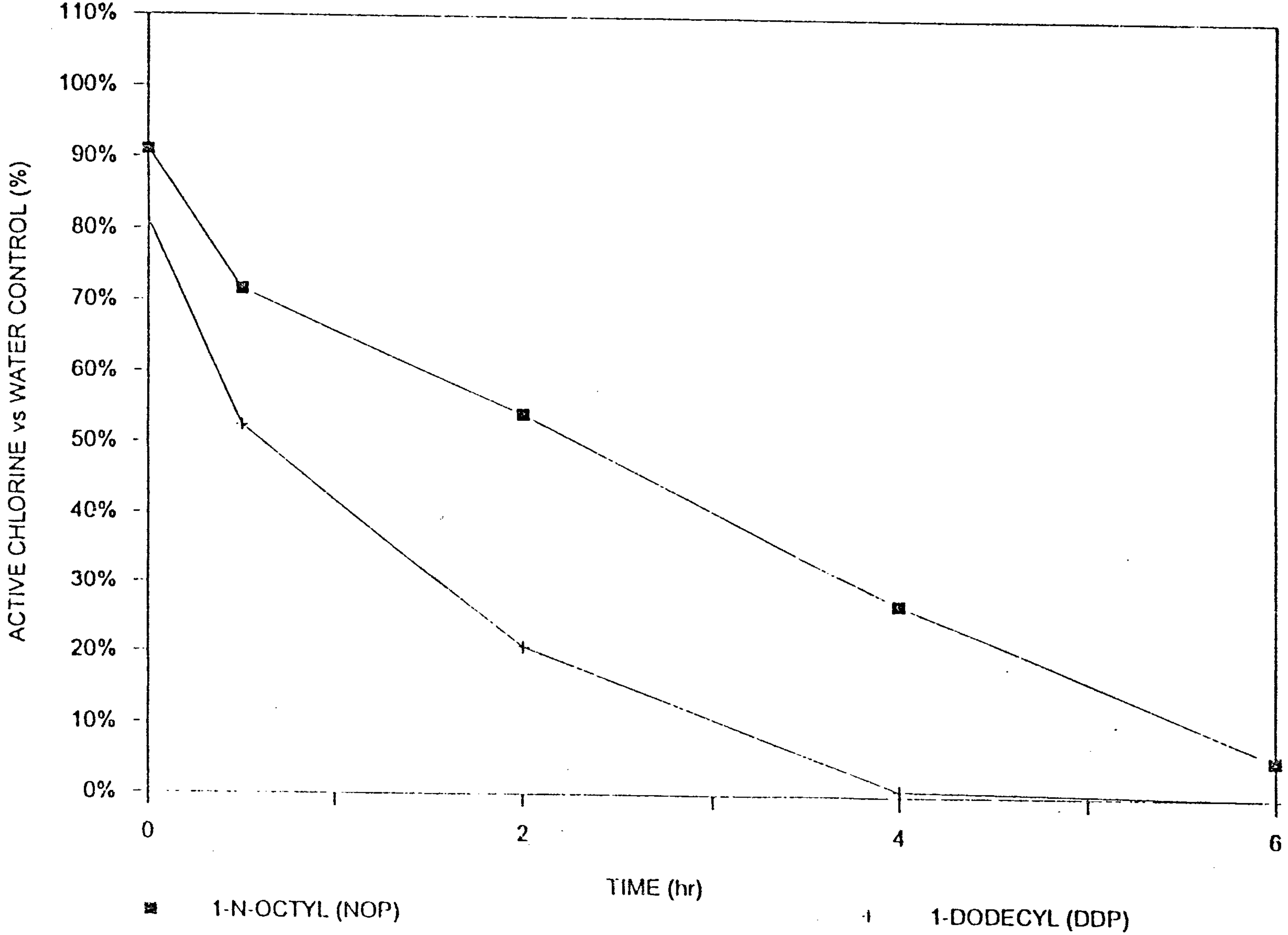

Figure C-2. Oxidative stability of partially soluble pyrrolidinones.

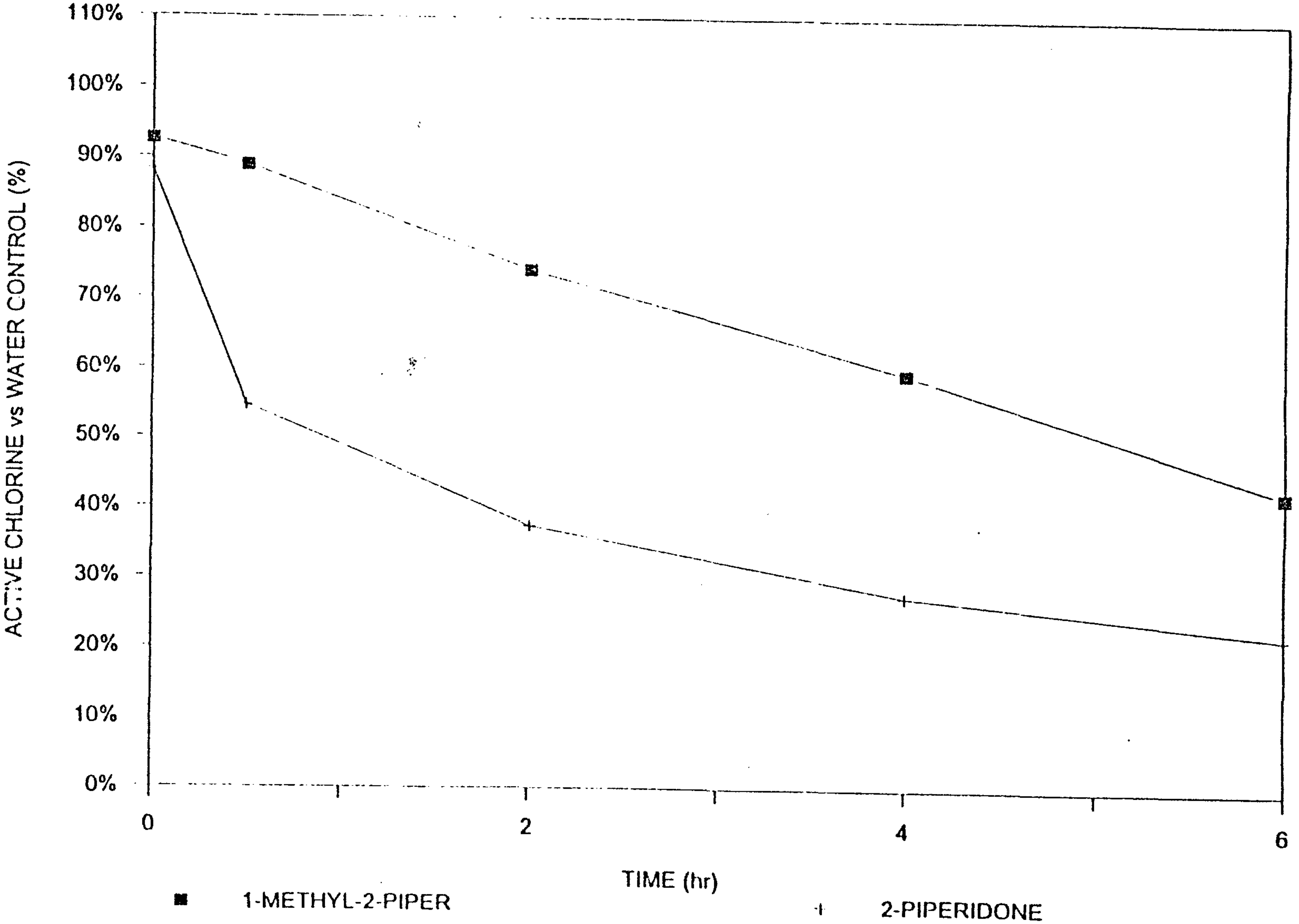

Figure C-3. Oxidative stability of piperidones.

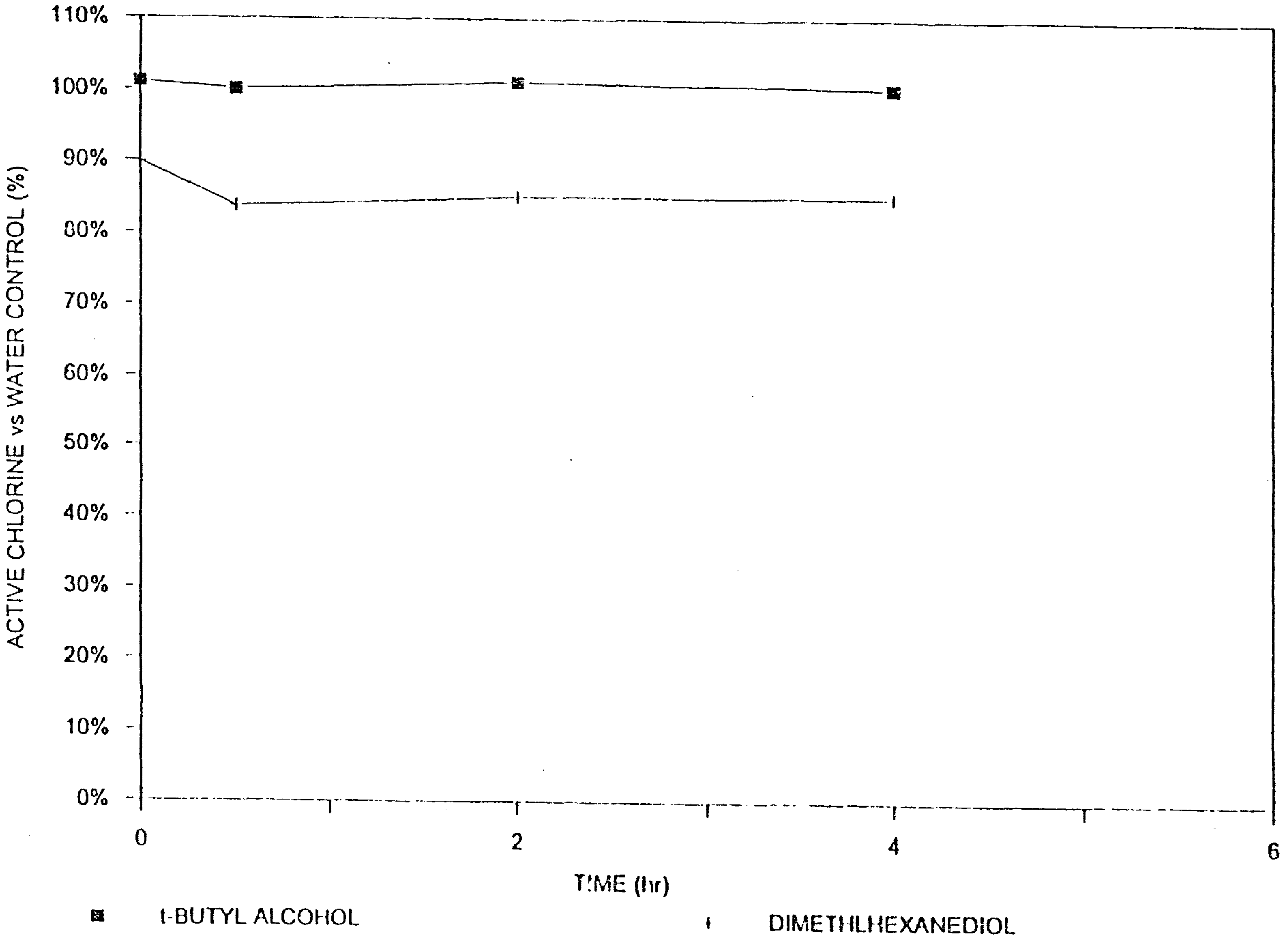

Figure C-4. Oxidative stability of tertiary alcohols.

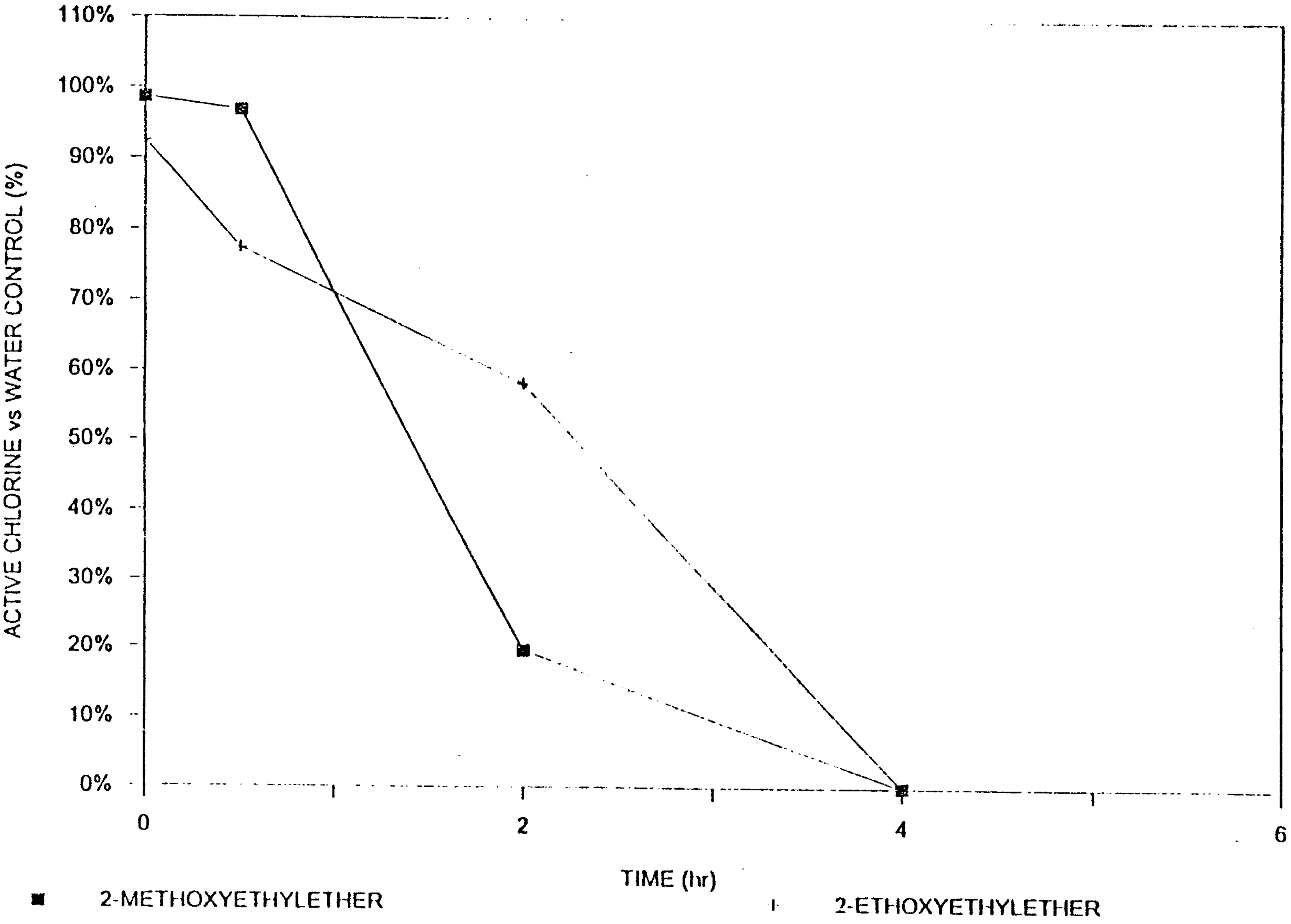

Figure C-5. Oxidative stability of diethylene glycol ethers.

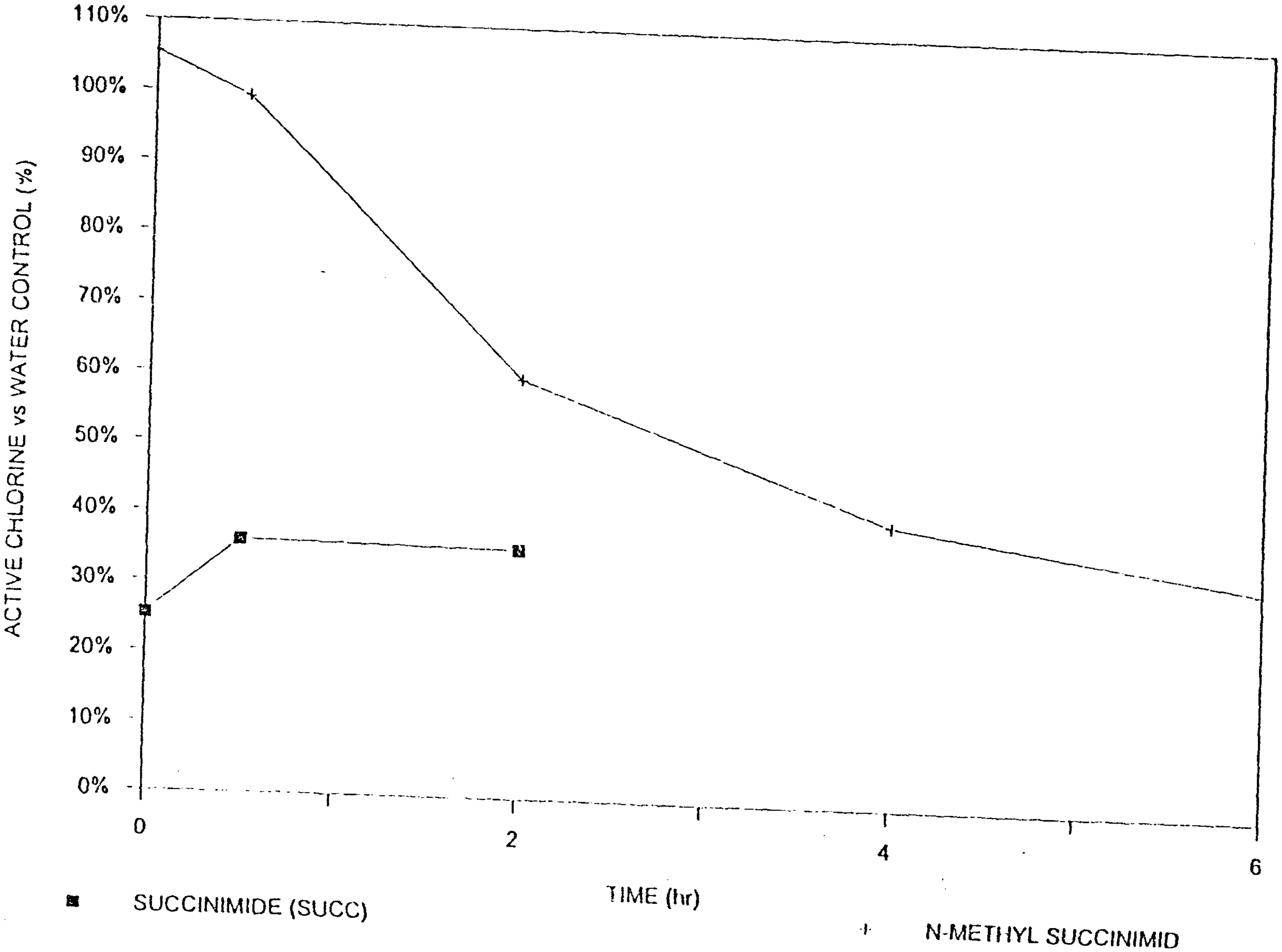

Figure C-6. Oxidative stability of succinimides.

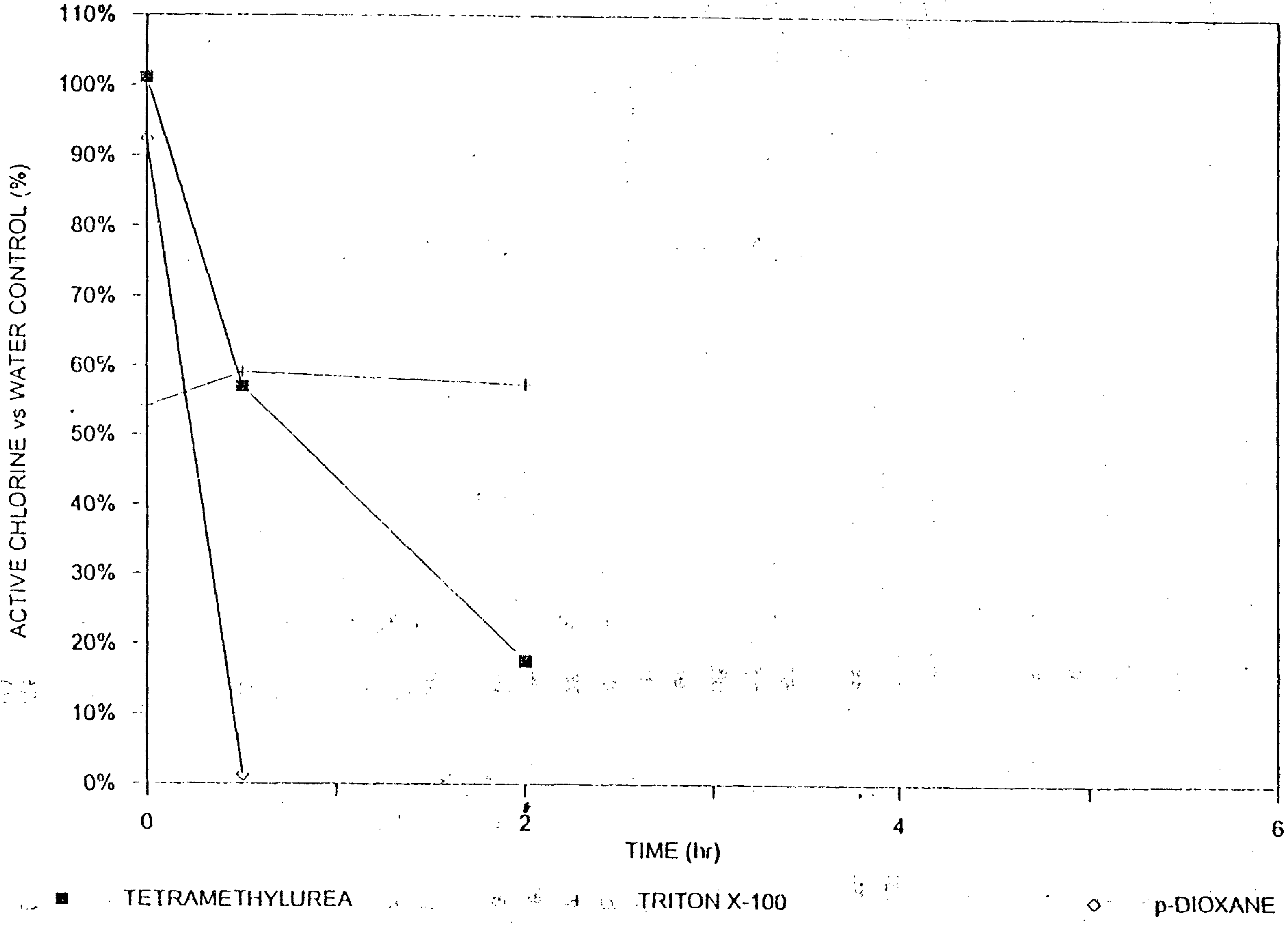

Figure C-7. Oxidative stability of other solvents.

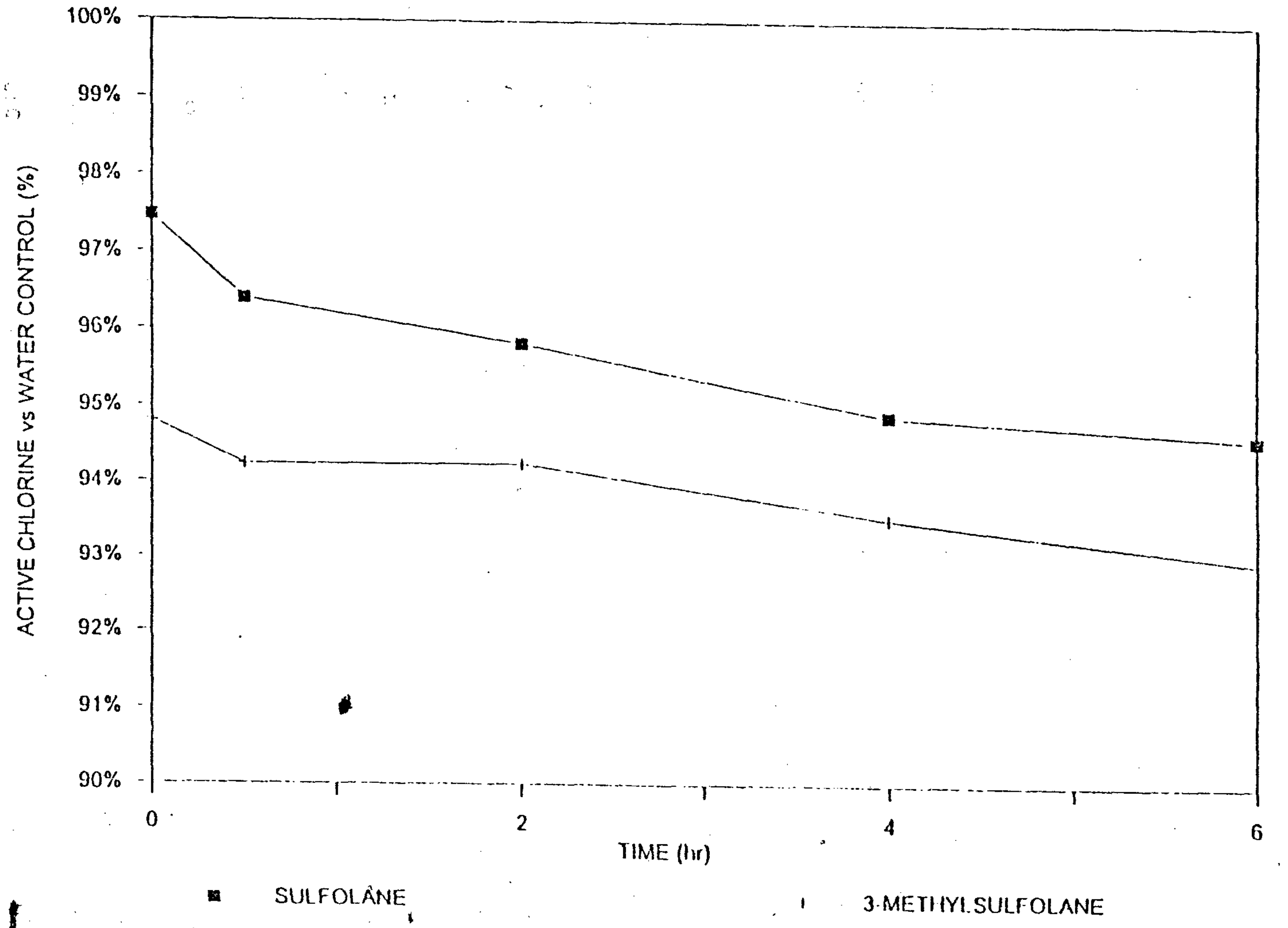

Figure C-8. Oxidative stability of sulfolanes.

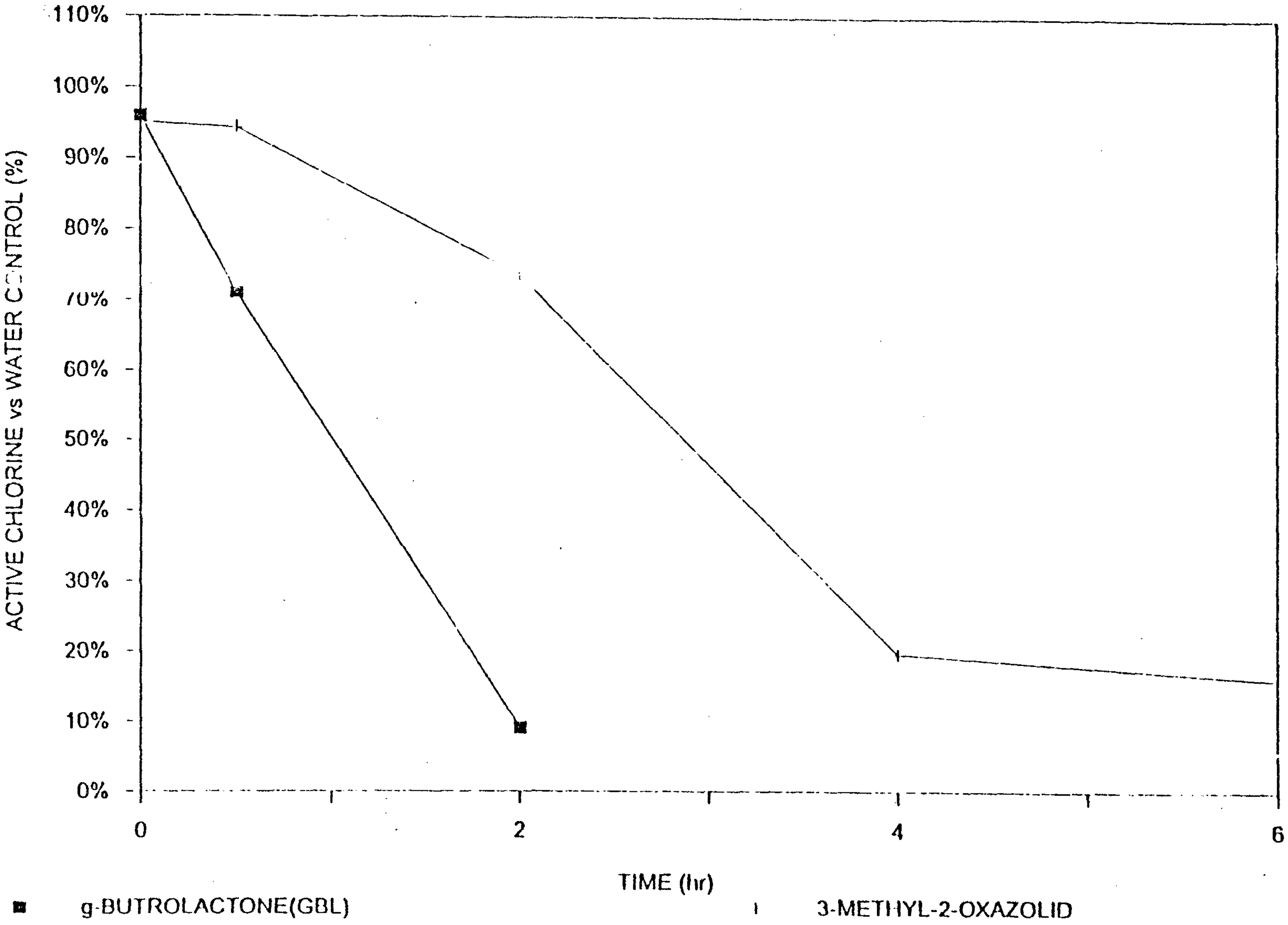

Figure C-9. Oxidative stability of lactones.

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APPENDIX D

SYNTHETIC SCHEMES FOR THE PREPARATION OF 1-*t*-BUTYL-2-PYRROLIDINONE

The preparation of 1-*n*-butyl-2-pyrrolidinone from the sodium salt of 2-pyrrolidinone (from sodium hydroxide in an oil dispersion) and *n*-butylchloride was reported by W. Gaffield.[1] Yields in the order of 80% were obtained. A low (4%) yield of 1-*t*-butyl-2-pyrrolidinone using a high temperature/pressure process involving a copper exchanged NaY-zeolite (Linde SK-40) catalyst for the gas phase reaction of γ-butyrolactone and *t*-butylamine was reported by Hatada and Ono.[2] High temperature/pressure reaction of a lactone and an alkylamine is the classical method for producing *N*-substituted pyrrolidinones.[3]

A high (90% +) yield of *N*-*n*-octyl phthalimide by reaction of the alkylhalide with the potassium salt of phthalimide in DMF at 60°C was reported by Landini and Rolla.[4] This procedure appeared to be the most simple found, and it was chosen for an attempt at preparing the desired 1-*t*-butyl-2-pyrrolidinone.

Two methods were examined for ease of preparation of the required Na or K salts of 2-pyrrolidinone. The first involved azeotroptic dehydration of concentrated base solutions in rapidly stirred, refluxing toluene (Dean-Stark trap) to produce a fine dispersion of free base. After the correct amount of water had been removed, 2-pyrrolidinone was slowly added to the refluxing, stirred dispersion. A white precipitate of the toluene insoluble salt was formed. The completeness of conversion to the salt was monitored by the amount of water captured in the Dean-Stark trap. This procedure was found to be slow and very time consuming (3 days to produce 1 mL of the desired salt) and was abandoned.

A rapid procedure[5] was found which made use of the water affinity of anhydrous acetone. A highly concentrated base water solution (50% by weight or

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[1] Gaffield, William, *Org. Preps. and Procedures Int.*, 9(2), 49-52 (1977).

[2] Hatada, Kou, and Yoshio Ono, *Bull. Chem. Soc.*, Japan, 50(10), 2517-2521 (1977).

[3] Hort, Eugene V., and L. R. Andersen in *Kirk-Othmer, Encyclopedia of Chemical Technology*, Vol. 19, 499-520 (Third Ed.), John Wiley, New York (1982).

[4] Landini, Dario, and Franco Rolla, *Synthesis*, 389 (1976).

[5] *Acetylene Chemistry*, T. W. Reppe, PB Report 18, 852-5, C. A. Meyer & Co., Inc., New York, New York, pp. 129 (1949).

higher base) is added directly to a vigorously stirred solution of 2-pyrrolidinone in dry acetone. An insoluble precipitate of the salt is almost immediately formed with high yields of the salts being produced. Three experimental syntheses follow.

1. Reaction of 1-Potassium-2-pyrrolidinone with *t*-Butyl Chloride

a. Preparation of 1-Potassium-2-pyrrolidinone

One mol (85.11 g) of 2-pyrrolidinone (Aldrich Chemical Co.) was added to 450 mL dry acetone in a 500-mL conical flask while being vigorously agitated with a large stirring magnet. Sixty-five grams 85% pure KOH pellets were dissolved in 50-mL deionized water and cooled to room temperature. This solution was added rapidly to the 2-pyrrolidinone-acetone solution while maintaining the vigorous stirring for a period of 30 min. The thick suspension of salt formed was filtered (vacuum) and washed with two 50-mL portions of fresh, dry acetone. The filter cake was then compressed with dental dam until all the acetone possible was expressed. The filtering cake was broken up and placed in evaporating dish and dried to constant weight in a vacuum desiccator. At constant weight, 60.76 g (0.49 mol) of the 1-potassium-2-pyrrolidinone salt was found. This weight corresponds to a 49% yield. It was found that the potassium salt was somewhat soluble in the dry acetone.

b. Reaction of 1-Potassium-2-pyrrolidinone with *t*-Butyl Chloride

Dry potassium-2-pyrrolidinone salt, 66.47 g (0.540 mol) was suspended in 300 mL dry (stored over 3A molecular sieves) DMF in a 500-mL singleneck flask fitted with a magnetic stirrer and a 250-mL dropping funnel. This salt has a solubility of about 1 g in 10 mL DMF at room temperature. *tertiary*-Butylchloride 69.4 g, 81.6 mL (0.75 mol) was charged into the dropping funnel. The chloride was added to the stirred DMF-salt mixture at the rate of approximately 24 drops per minute requiring 90 min for completion. The mixture was stirred at room temperature for 16 hr. There was an obvious change in solution appearance after 4 hr as potassium chloride was formed and precipitated out of the otherwise clear solution.

After 16 hr reaction time, the solution was filtered, yielding 35.75 g of dry KCl. This amount corresponds to 89.0% of the theoretically expected amount. The DMF reaction solvent was removed by distillation through a 25-cm (10-in) Vigreux column at ambient pressure. During initial heating to the 154°C boiling point of DMF, a substantial amount of outgassing of a noncondensible substance was noted. This gas had the distinct odor of isobutylene (2-methylpropene) indicating dehydrohalogenation of the *tertiary*-butylchloride by strong base. The highest pot temperature reached was 230°C at which time no distillate was being received. The residue remaining in the distillation flask weighed only 35.5 g, well below the theoretical yield of 66.53 g (0.54 mol). Distillation of this residue at 35 mmHg, using a single 13-cm (5-in) Vigreux column, showed the residue to be nearly all 2-pyrrolidinone by IR spectra. Evidently, little or none of the desired 1-*t*-butyl-2-pyrrolidinone was formed. Side reactions dominated.

2. Reaction of 1-Sodium-2-pyrrolidinone with *t*-Butyl Chloride

a. Preparation of 1-Sodium-2-pyrrolidinone

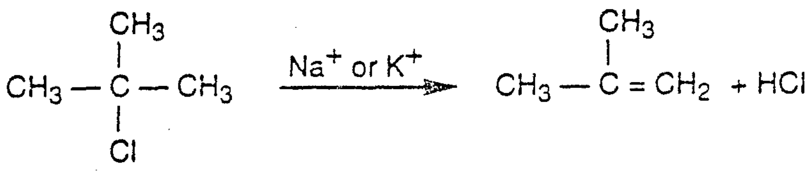
Four-tenths of a mole (16.00 g) of sodium hydroxide pellets was dissolved in 16.0 mL deionized water and cooled to room temperature. Thirty-four (34.00) grams 2-pyrrolidinone was dissolved in 400 mL dry acetone in a rapidly stirred 500-mL conical flask. The sodium hydroxide was then rapidly poured into the 2-pyrrolidinone-acetone solution. A voluminous white precipitate was immediately formed. After stirring for 30 min, the suspension was filtered, washed, compressed, and dried, as was done with the potassium salt. At constant weight, 42.75 g (0.398 mol) of salt was produced with the yield being nearly stoichiometric.

b. Reaction of 1-Sodium-2-pyrrolidinone with *t*-Butyl Chloride

The reaction time (at room temperature) was extended to 96 hr because the sodium salt had only about 1/8 the solubility in dry dimethylformamide (DMF) exhibited by the potassium salt. Filtering of the reaction mixture yielded 30.76 g (95.9% of theory) of dry sodium chloride. Distillation of the filtrate to strip off the DMF solvent indicated that there was some dehydrohalogenation of the *t*-butyl chloride as the distinct odor of isobutylene (2-methylpropene) was quite evident. Completion of the distillation, at ambient pressure, up to a pot temperature of 227°C yielded a residue of 34.89 g. At this point it was evident that the reaction had not proceeded as desired. The theory yield (0.55 mole) of 1-*t*-butyl-2-pyrrolidinone is

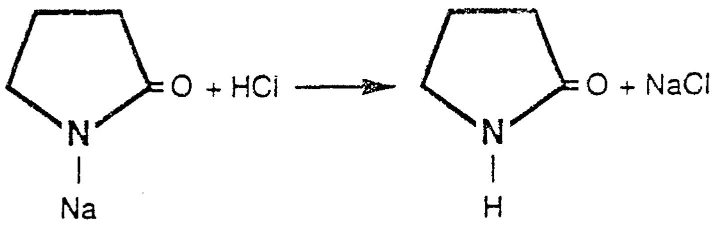
77.67 g, over twice the weight of the pot residue. Vacuum (44 mmHg) distillation of this residue yielded a middle fraction (19.64 g) boiling at 155° to 158°C (44 to 46 mmHg). This boiling range corresponds to that of 2-pyrrolidinone. An infrared spectrum of this fraction confirmed that it was, indeed, 2-pyrrolidinone. If any of the desired 1-*t*-butyl-2-pyrrolidinone was produced it was present only in trace amounts. At this point it was evident that the desired reaction was not taking place; instead, two side reactions were occurring:

1. **Dehydrohalogenation:**



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{\overset{|}{\underset{|}{C}}}}-CH_3 \xrightarrow{Na^+ \text{ or } K^+} CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2 + HCl$$

2. **Salt Neutralization:**



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These two reactions were rather rapid. The odor of isobutylene (2-methylpropane) confirms the first reaction. The second reaction was confirmed as the major distillation fractions were 2-pyrrolidinone and that nearly stoichiometric quantities of potassium or sodium chloride were found.

The tertiary halides are more subject to dehydrohalogenation than primary and secondary halides. Apparently the choice of solvent, DMF, also had an accelerating effect on the dehydrohalogenation reaction.

3. Reaction of 1-Lithium-2-Pyrrolidinone with *t*-Butyl Chloride

An alternate synthesis scheme was examined which involved the use of *n*-butyllithium (CH_3-CH_2-CH_2-CH_2-Li) in cyclohexane to form 1-lithium-2-pyrrolidinone anhydrously. The cyclohexane solvent is nonpolar and aprotic, quite different from DMF. The lithium atom is much smaller than either sodium or potassium, and its reactivity with *t*-butyl chloride should be higher. The following procedures were used in this attempted synthesis:

A 500-mL three-necked flask, a condenser, valved gas inlet, a dropping funnel, and magnetic stirring bar were oven dried at 130°C for 4-hr, assembled hot, and flushed with dry nitrogen to cool. These procedures are necessary because *n*-butyllithium is pyrophoric and very reactive, even with absorbed water.

The top of the dropping funnel was fitted with a rubber injection septum. One hundred fifty milliliters of dried (over 3A molecular sieves) cyclohexane and 3.40 g redistilled 2-pyrrolidinone were charged into the reaction flask and stirring was initiated. A slow wash of dry nitrogen was maintained. Gas flow was monitored with a "U" tube bubbler at the gas outlet. Twenty mL of 2 molar *n*-butyllithium was transferred via an oven dried 25-cc glass syringe and an 18-gauge, 6-in long needle from the "Sure Seal" closed reagent bottle (Aldrich Chemical Company) to the addition funnel. The *n*-butyllithium was added at a slow (≅ 10 drops/min) rate into the stirred reaction mixture requiring 30 min for complete addition. Evolution of *n*-butane was immediate as indicated by an increased bubble rate in the "U" gas flow indicator. Formation of the salt was readily observable as a white, thick precipitate. This mixture was stirred overnight while under a dry N_2 atmosphere. The dropping funnel was flushed with two 20-mL portions of dry cyclohexane, and 0.044 mole (10% excess, 4.07 g) t-butyl chloride in 20 mL dry cyclohexane was charged into the dropping funnel. This mixture was added over a 30-min period to the stirred reaction mixture. A slow flush of dry nitrogen was maintained over this stirred mixture for 24 hr. During this time, there was no apparent change in the mixture's appearance from a slurry of white flaky precipitate particles in a light yellow fluid. There was no appearance of crystalline lithium chloride.

After 24 hr stirring at room temperature, the reaction flask was transferred to a rotary vacuum evaporator and solvent stripped off at 60°C and 50 mmHg pressure. The dried residue was a fluid free, dry white powder. The powder weighed 3.82 g. If only the unreacted 1-lithium-2-pyrrolidinone remained, the product should have weighed 3.64 g. It was apparent that the product was mostly the 1-lithium-2-pyrrolidinone and perhaps some sorbed solvent or lithium chloride. As there was little if any fluid present it must be concluded that none of the desired 1-t-butyl-2-pyrrolidinone was found.

It must be understood that the change of reaction solvent to cyclohexane converted the reaction from homogeneous (the pyrrolidinone salts have some solubility in DMF) to heterogeneous because the 1-lithium-2-pyrrolidinone salt probably has little solubility in cyclohexane. Apparently there was no reaction with the *t*-butyl chloride. The use of a phase-transfer catalyst (PTC) may be useful in making this preparative reaction viable.