A preliminary investigation of clathration for the separation of monoterpenes
by Gajendrakumar Prabhudas Dubal

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Chemical Engineering
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Abstract:
The purpose of this investigation was to study the application of the clathration technique to the separation of monoterpene hydrocarbons particularly alpha-pinene, beta-pinene, delta.-3-carene and dipentene.

The experimental procedure consisted of bringing a terpene-amine feed mixture into contact with a complexing agent. This resulted in the precipitation of a clathrate, which was then filtered, dried and dissolved in 1:1 hydrochloric acid to separate out the clathrated terpenes as a hydrocarbon phase. The filtrate containing unclathrated terpenes was discarded. The hydrocarbon phase was extracted with n-pentane and washed twice with 1:1 hydrochloric acid. The terpene feed mixture and the clathrated terpenes were analyzed on a gas chromatograph. The variation of this scheme included varying clathration temperature, drying the clathrate completely following filtration, varying feed to complex weight ratio and varying feed composition and constituents.

About 88 complexes were tried at room temperature for the separation of three feed mixtures consisting of different terpenes mentioned earlier. In 46 cases, clathration took place and the analysis of the clathrated terpenes indicated that several complexes had fair selective clathrating ability for delta-3-carene and dipentene depending upon the presence of other terpenes in the feed. Concentration of these two terpenes increased by 5 to 10 % from the feed to the clathrate. Other previously mentioned variables did not radically change the selectivity of most of complexes.

However, nickel(4-methylpyridine)2(thiocyanate)2, a complex, exhibited an excellent selective clathrating ability for myrcene when clathration is carried out at 5°C. Myrcene was present as an impurity in beta-pinene and that to the extent of 6.25 %. In a single clathration stage, this complex concentrated myrcene from 2 % in the feed to 61 % in the clathrated terpenes. An increase in the feed to complex ratio increased the proportion of myrcene in the clathrate, up to a certain limit. Similarly, an increase in the proportion of myrcene in the feed increased its proportion in the clathrate, Myrcene was concentrated from 25 % in the feed to about 90 % in the clathrate in one clathration stage.

Boiling points of beta-pinene (164-6°C) and myrcene (167°C) are very close and therefore, difficult to separate . by fractional distillation. It is apparent that they can be separated by the clathration technique.

A PRELIMINARY INVESTIGATION OF CLATHRATION FOR THE SEPARATION OF MONOTERPENES

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A thesis submitted to the Graduate Faculty in partial
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Boiling points of beta-pinene (164-6 °C) and myrcene (167 °C) are very close and therefore, difficult to separate by fractional distillation. It is apparent that they can be separated by the clathration technique.

INTRODUCTION AND THEORY

The purpose of this investigation was to study the application of the clathration technique to the separation of monoterpene hydrocarbons, particularly, alpha-pinene, beta-pinene, delta-3-carene and dipentene.

All these terpenes have the same molecular formula $C_{10}H_{16}$ but different structural formulas. Their boiling points are 156.2, 164-6, 167 and 170.3 °C respectively.

These terpenes occur in nature as odorous substances in the flowers, fruits, leaves and roots of many plants. Alpha-pinene is very widely distributed in nature, being found in most essential oils. It is the main constituent of oil of turpentine. Beta-pinene and delta-3-carene accompany alpha-pinene in most sources of alpha-pinene, but in smaller proportions. The optically active limonene is found in both dextro and levo forms in several essential oils e.g. lemon, orange and caraway oils. The racemic variety of limonene, known as dipentene, occurs in various turpentine oils. These hydrocarbons are separated from the oils by fractional distillation and/or via certain crystalline adducts. The individual hydrocarbon is then separated by careful fractional distillation.

Alpha-pinene, beta-pinene, delta-3-carene and dipentene have some industrial importance, though not necessarily as pure chemical individuals. The importance of alpha-pinene lies in its conversion to alpha-terpineol -used for the commercial manufacture of perfumes- and to bornyl derivatives and camphene for the production of camphor. Beta-pinene can be converted to myrcene whose tendency to polymerize has been used to some extent in the preparation of rubber-like polymers and copolymers.

The clathration technique involves selective removal of a specific component from a mixture by the formation of a molecular compound or clathrate between a complex and the component. The clathrate is then separated from the reaction mixture and the clathrated compound recovered.

A clathrate is one kind of inclusion compound which consists primarily of two molecular species, one of which (host) provides space in its structure in which molecule(s) of the other (guest) is completely enclosed. Using X-ray diffraction and other techniques, Powell(1) has shown that the benzene molecule is completely enclosed in the three-dimensional structure of nickel-cyanide-amino complex. He proposed that this type of compound be called clathrate compounds from Latin "Clathratus" meaning enclosed or protected by cross bars of a grating.

The interaction between the host and the guest molecules is generally quite weak and the bonds being of the van der Waals type.(2) Therefore, decomposition of a clathrate, that is, breaking of the host structure, can occur by simple means such as melting, sublimation or dissolution. Since the interaction energy between the host and the guest is weak, the molecular structure and properties of the separated material are not affected throughout this process of separation or purification.

One class of the host molecules includes Werner complexes. From the view point of separation or purification, these complexes are most interesting since many of them are reported as having remarkable clathrating ability.(3,4,5) A Werner complex has three constituents viz. a metal atom like nickel, cobalt etc., a nitrogen base compound like substituted pyridines and an anion like thiocyanate, chloride etc.

Many investigators(3,4,5) have worked on Werner complexes for separating aromatic hydrocarbons of the benzene series and they have been particularly successful in separating C_8H_{10} aromatic hydrocarbon isomers. Schaeffer et al.(3)

investigated at least one complex with a remarkable selectivity for each of the four C_8 aromatic isomers. In a single stage concentration increased from feed to product of 19.9 to 75.9 volume % for p-xylene, 45.5 to 56.9 volume % for m-xylene, 19.3 to 53.1 volume % for o-xylene and 15.3 to 54.6 volume % for ethylbenzene. They(3) have also reported a complex, able to clathrate p-xylene selectively from an aromatic -rich gasoline.

The reported complexes are very rapidly formed when the appropriate reagents are mixed at room conditions. Reaction time is well under one minute and yield is almost quantitative.

There are several methods of forming a clathrate. These include:

(1) Simple contact of the feed mixture with the complex with or without stirring.

(2) Contacting the feed material with a hot solution of the complex followed by cooling to form the solid clathrate.

(3) Contacting the feed material with a suspension of the complex. The fluid in which the complex is suspended is an organic liquid which will not enter into the clathration.

(4) Adding the metal thiocyanate or other complexing agent to the amine-feed mixture.

There are several methods of recovering the desired component from the solid clathrate. These include:

(1) Decomposition of the clathrate with a mineral acid thus releasing the clathrated component.

(2) Steam stripping.

(3) The clathrate is dissolved in a hot solvent and the desired constituent removed by extraction and/or distillation.

Most of the investigators have been working on separating aromatic compounds by clathration technique. However, the number of possible compounds which might be studied for clathration is at least several thousand and possibly much larger. The present investigation was carried out, for the first time, to study the clathration of monoterpene hydrocarbons.

The clathration technique for separating isomers seems to have some definite advantages over the commonly used methods. It has a real advantage when the isomers (or compounds) have very close boiling points. In a situation like this, one clathration stage can give the same separation as a distillation column with hundreds of plates. It also has advantages from a product quality standpoint. For example, ultra-pure benzene has been prepared by clathration. The clathration method, when it is used commercially, will probably be used to obtain high purity chemical intermediates not now being produced in any volume.

The process is new. There are no commercial plants and no announced plans for building a clathration plant. It is still so new that much engineering and pilot work must be done before the process proves itself. If and when it does prove itself there will probably be many applications for the process in the petrochemical industry as new intermediates are developed which can not be separated from refinery streams by existing commercial methods.

RESEARCH OBJECTIVES

The purpose of this investigation was to study the application of the clathration technique to the separation of monoterpene hydrocarbons such as alpha-pinene, beta-pinene, delta-3-carene and dipentene from their mixtures. Werner type of complexes were to be used as clathrating agents. The effect of variables such as clathration temperature, feed to complex ratio, feed compositions and constituents, drying of the clathrate, etc. on the selective clathrating abilities of the complexes were to be studied.

EXPERIMENTAL DETAILS

Werner complexes have the general formula of $M(N)_x(A)_2$ where "M" is a metal atom, usually bivalent, "N" a nitrogen base compound and "A" an anion, usually monovalent. In most cases, "x" is 4, but it can be 2 also.

All complexes in this investigation were prepared employing stoichiometric amounts of reactants except that a 12.5 mole % excess of nitrogen base was usually added to ensure a quantitative yield. The various complexes were tried for clathration by variation of a basic method. The basic method may be exemplified as follows.

23.8 gms. (0.1 gm-mole) of nickelous chloride hexahydrate was dissolved in approximately 300 mls. of water and 19.4 gms. (0.2 gm-mole) of potassium thiocyanate was added to give a solution of nickel thiocyanate. 41.8 gms. (0.45 gm-mole, 12.5 mole % in excess) of 4-methylpyridine was dissolved in 50 mls. of terpene feed mixture. This amine-feed mixture was then added to the solution of nickel thiocyanate and a blue precipitate of the clathrate appeared immediately. As noted earlier, the reaction was very rapid and the yield almost quantitative. The reaction mixture was then filtered, the clear and colorless filtrate containing unclathrated terpenes was discarded. The blue residue on the filter was removed and air-dried in certain cases.

The blue precipitates were dissolved in approximately 200 mls. of 1:1 hydrochloric acid to break the clathrate. This resulted in two phases, viz. hydrocarbon and aqueous. The hydrocarbon phase which separated was extracted with a small amount of n-pentane. After separation of liquid phases, the hydrocarbon phase was washed twice with 1:1 hydrochloric acid and then analyzed by means of a gas chromatograph.

The variation of this scheme included varying temperature at which the clathration took place, drying the clathrate completely following filtration, varying the complex to feed ratio, washing the clathrate with n-pentane to remove unclathrated terpenes, varying feed composition and constituents.

In this investigation, the following different constituents of complex $M(N)_x(A)_2$ were studied.

Metal atom (M) :

1. Nickel
2. Cobalt
3. Zinc
4. Cadmium
5. Manganese
6. Iron

Nitrogen base compound (N) :

1. 2-Methylpyridine
2. 3-Methylpyridine
3. 4-Methylpyridine
4. Pyridine
5. o-Toluidine
6. n-Hexylamine

7. 2,6 Lutidine
8. 3,4 Lutidine
9. Indole
10. Acridine
11. n-Methylpiperazine
12. Hydroxyethylpiperazine
13. Aminoethylpiperazine
14. 2,6-Dimethylpiperazine
15. 2-Methyl-5-ethyl-pyridine
16. N-isopropylbenzylamine
17. N,N-Dimethyl-p-toluidine
18. 4-isopropylpyridine
19. 1,8-p-Menthanediamine
20. Pyrrolidine
21. 4-Methylpiperidine

Anion (A) :

1. Thiocyanate
2. Chloride
3. Formate
4. Nitrate

A gas chromatograph with thermal conductivity detection, manufactured by Wilkens Instrument and Research, Inc., (model: Aerograph 200) was employed to analyze the terpenes. The pertinent details are as follow(7):

Column liquid : β,β'-Oxydipropionitrile.

Solid support : Diatomaceous earth, acid-washed
Chromsorb P, 60-80 mesh.

Liquid to support weight ratio : 15:100

Carrier gas : Hydrogen

Hydrogen flow rate : below 60 mls./min.

Gas inlet pressure : 70 psig.

Column temperature : 90-100 °C

Detector temperature : 145-150 °C

Injector temperature : 120-130 °C

Column : (1) 10 ft. and (2) 15 ft. length 5/32 inch I.D. copper coiled.

Sample size : less than 3 microliters.

Most of the analytical work was done on column of 10 ft. length but afterwards, a new column of 15 ft. length was prepared keeping other factors constants. Better and more reliable analytical results were obtained with the longer column.

At one stage during this investigation, infra-red spectroscopy was employed in identifying myrcene in the clathrated terpenes.

RESULTS AND DISCUSSION

If the whole research work is considered as made of several parts or stages, it would be proper to discuss one part after another in the same order as they were carried out. In most cases, results obtained in one part furnish the basis for the subsequent part. Therefore, the present discussion would be more clear if each part is considered one by one followed by a final overall discussion.

Part I :

30 different complexes were tried for clathration with a feed mixture having an approximate composition of :

alpha-pinene	29 weight %
beta-pinene	29 weight %
delta-3-carene	42 weight %

Table 1 shows all the complexes tried with this feed mixture and the composition of the clathrated terpenes in the cases where clathration took place. All complexes were tried at room temperature following the previously described basic method completely.

In 15 cases, precipitates of the clathrate were not observed which might be because of the failure of either the complex itself or the clathrate formation. About five complexes

Table 1. Initial Investigation on Clathration

	Weight % of		
	Alpha-pinene	Beta-pinene	Delta-3-carene
Feed	29.0	29.0	42.0
Complex*	In clathrated terpenes		
1. Ni(4-MePy)$_4$(SCN)$_2$	16.3	19.5	64.1
2. Ni(3-MePy)$_4$(SCN)$_2$	20.0	19.8	60.2
3. Ni(4-MePy)$_2$(SCN)$_2$	33.0	6.4	61.0
4. Ni(Py)$_4$(SCN)$_2$	21.3	34.4	44.1
5. Ni(o-Tn)$_4$(SCN)$_2$	28.1	18.3	53.6
6. Ni(2Me,5Et Py)$_4$(SCN)$_2$	20.2	25.6	46.2
7. Ni(n-Hx)$_4$(SCN)$_2$	22.0	15.2	63.0
8. Ni(3,4 Ln)$_4$(SCN)$_2$	33.4	24.0	42.5
9. Ni(n-MePz)$_4$(SCN)$_2$	39.4	25.7	34.8
10. Co(3,4 Ln)$_4$(SCN)$_2$	22.6	15.8	61.6
11. Ni(n-Me Pz)$_4$(Ft)$_2$	31.2	29.6	39.2

(continued)

* Abbreviation used in all Tables:

Ac	acridine	Am	amino	Bz	benzylamine
Et	ethyl	Ft	formate	Hx	hexylamine
Hy	hydroxy	In	indole	Ln	lutidine
Me	methyl	Md	menthanediamine	Pd	piperidine
Pl	pyrrolidine	Pr	propyl	Py	pyridine
Pz	piperazine	Tn	toluidine		

Table 1 (continued)

Complex	Alpha-pinene	Beta-pinene	Delta-3-carene
12. $Zn(4\text{-}MePy)_4(SCN)_2$	31.6	28.0	40.3
13. $Cd(4\text{-}MePy)_4(Ft)_2$	28.8	26.5	44.7
14. $Cd(4\text{-}MePy)_4(SCN)_2$	31.2	27.4	41.7
15. $Mn(4\text{-}MePy)_4(SCN)_2$	33.0	27.0	40.0
16. $Ni(2\text{-}MePy)_4(SCN)_2$	--	--	--
17. $Ni(4\text{-}MePy)_4Cl_2$	--	--	--
18. $Ni(Py)_4Cl_2$	--	--	--
19. $Ni(2,6\ Ln)_4(SCN)_2$	--	--	--
20. $Ni(In)_4(SCN)_2$	--	--	--
21. $Ni(Ac)_4(SCN)_2$	--	--	--
22. $Co(4\text{-}MePy)_4(SCN)_2$	--	--	--
23. $Co(Py)_4(SCN)_2$	--	--	--
24. $Co(2Me,5Et\ Py)_4(SCN)_2$	--	--	--
25. $Co(n\text{-}MePz)_4(SCN)_2$	--	--	--
26. $Ni(4\text{-}MePy)_4(Ft)_2$	--	--	--
27. $Ni(4\text{-}MePy)_2(Ft)_2$	--	--	--
28. $Ni(2Me,5Et\ Py)_4(Ft)_2$	--	--	--
29. $Ni(3,4\ Ln)_4(Ft)_2$	--	--	--
30. $Zn(n\text{-}MePz)_4(SCN)_2$	--	--	--

showed good selectivity towards delta-3-carene as is clear from the increase of up to 22 % for delta-3-carene from the feed to the clathrate.

Part II :

However, it was essential to check and reproduce the results of Part I before arriving at a definite conclusion. Therefore, five promising complexes of Part I along with nine other complexes were tried for the clathration with a feed mixture having approximate composition:

alpha-pinene	33.3	weight %
beta-pinene	33.3	weight %
delta-3-carene	33.3	weight %

When the clathrate is not thoroughly dried following filtration, as was common in Part I, there is a possibility of unclathrated terpenes sticking to the clathrate and the result may be erroneous both quantitatively and qualitatively. Therefore, to avoid such a possibility, all the clathrates in Part II were washed thoroughly with n-pentane, filtered and dried. It was reasonable to assume that all the unclathrated terpenes sticking to the clathrate would be removed along with n-pentane in the filtrate and results would be more reliable.

Table 2 shows the complexes tried and analysis of the clathrated terpenes in the cases where the clathration took place. Some complexes which had shown good selective clathrating ability towards delta-3-carene as noted in Table 1, showed fair selectivity towards delta-3-carene. This might be the result of avoiding possibility of unclathrated terpenes sticking to the clathrate. However, the feed compositions in Part I and Part II were slightly different and this might have an influence on the composition of the clathrated terpenes. So, one complex, shown at the bottom of Table 2, was tried with the feed having a composition very close to that in Part I. The result indicated that feed composition did not exert any remarkable influence on the composition of the clathrated terpenes.

From the results of Part I and Part II, it is concluded that several complexes, which gave the clathrate, have shown fair selective clathrating ability for delta-3-carene. There is an increase of 4 to 5 % in the delta-3-carene content from the feed to the clathrate.

Part III :

Forty different complexes were tried for the clathration with a feed mixture having an approximate composition

Table 2. Initial Investigation on Clathration

	Weight % of		
	Alpha-pinene	Beta-pinene	Delta-3-carene
Feed	33.3	33.3	33.3
Complex	In clathrated terpenes		
1. Ni(4-MePy)$_4$(SCN)$_2$	31.4	31.7	37.0
2. Ni(3-MePy)$_4$(SCN)$_2$	30.6	32.2	37.2
3. Ni(4-MePy)$_2$(SCN)$_2$	32.5	29.9	37.6
4. Ni(n-Hx)$_4$(SCN)$_2$	32.2	29.2	38.5
5. Co(3,4 Ln)$_4$(SCN)$_2$	32.1	30.7	37.2
6. Cd(4-MePy)$_4$(Ft)$_2$	31.2	31.2	37.6
7. Ni(n-MePz)$_4$(SCN)$_2$	31.5	31.1	37.4
8. Ni(Pl)$_4$(NO$_3$)$_2$	31.3	30.2	38.5
9. Ni(4-MePy)$_4$(NO$_3$)$_2$	--	--	--
10. Ni(4-MePy)$_2$(NO$_3$)$_2$	--	--	--
11. Ni(3,4 Ln)$_4$(NO$_3$)$_2$	--	--	--
12. Ni(n-Hx)$_4$(NO$_3$)$_2$	--	--	--
13. Ni(2Me,5Et Py)$_4$(NO$_3$)$_2$	--	--	--
14. Ni(Py)$_4$(NO$_3$)$_2$	--	--	--
Feed	30.0	30.0	40.0
Complex	In clathrated terpenes		
1. Ni(4-MePy)$_2$(SCN)$_2$	28.7	28.5	42.8

of :

alpha-pinene	33.3 weight %
delta-3-carene	33.3 weight %
dipentene	33.3 weight %

Table 3 shows all the complexes tried with this feed mixture and the composition of the clathrated terpenes in twenty-one cases where clathration took place. For other nineteen cases, one of the following is true: (1) Either the complex or the clathrate was not formed. (2) Amount of terpenes in the clathrate was so small, just few drops, that proceeding further was thought of little importance.

All the forty complexes in this part were studied at room temperature employing the previously described basic method with stirring.

From the result of this part, it is concluded that all the twenty-one complexes, which gave the clathrate, have shown fair selective clathrating ability for dipentene. These complexes have been able to increase the content of dipentene up to 11 % from the feed to the clathrate.

Part IV :

Since beta-pinene and delta-3-carene have very

Table 3. Initial Investigation on Clathration

		Weight % of	
	Alpha-pinene	Delta-3-carene	Dipentene
Feed	33.3	33.3	33.3
Complex	In clathrated terpenes		
1. $Ni(4\text{-}MePy)_4(SCN)_2$	23.2	34.7	42.0
2. $Ni(4\text{-}MePy)_2(SCN)_2$	27.2	33.1	39.1
3. $Ni(2Me,5Et\ Py)_4(SCN)_2$	24.0	34.8	41.2
4. $Ni(3,4\ Ln)_4(SCN)_2$	28.2	34.0	37.8
5. $Ni(n\text{-}MePz)_4(SCN)_2$	23.2	33.4	43.5
6. $Ni(Hy\ Et\ Pz)_4(SCN)_2$	27.0	33.0	40.0
7. $Co(3,4\ Ln)_4(SCN)_2$	25.4	33.1	41.4
8. $Zn(3,4\ Ln)_4(SCN)_2$	20.0	35.7	44.2
9. $Cd(4\text{-}MePy)_4(SCN)_2$	31.2	30.6	38.3
10. $Cd(3,4\ Ln)_4(SCN)_2$	30.0	33.7	36.2
11. $Mn(4\text{-}MePy)_4(SCN)_2$	30.6	31.4	38.0
12. $Zn(4\text{-}MePy)_4(Ft)_2$	29.2	32.4	38.4
13. $Ni(4\text{-}MePy)_4Cl_2$	30.6	31.4	38.1
14. $Co(4\text{-}MePy)_4Cl_2$	29.8	32.0	38.2
15. $Cd(4\text{-}MePy)_4Cl_2$	27.8	33.0	39.2
16. $Zn(4\text{-}MePy)_4Cl_2$	29.8	33.5	36.7
17. $Co(4\text{-}iso\text{-}PrPy)_4(SCN)_2$	37.2	28.7	34.1
18. $Ni(1,8\ p\text{-}Md)_4(SCN)_2$	25.5	35.4	39.1

(continued)

Table 3 (continued)

Complex	Alpha-pinene	Delta-3-carene	Dipentene
19. $Co(1,8\ p\text{-}Md)_4(SCN)_2$	26.4	34.0	39.6
20. $Fe(4\text{-}MePy)_4(SCN)_2$	28.8	34.7	46.5
21. $Fe(3,4\ Ln)_4(SCN)_2$	26.1	33.4	40.4
22. $Ni(o\text{-}Tn)_4(SCN)_2$	--	--	--
23. $Ni(n\text{-}Hx)_4(SCN)_2$	--	--	--
24. $Ni(Am\ Et\ Pz)_4(SCN)_2$	--	--	--
25. $Co(2Me,5Et\ Py)_4(SCN)_2$	--	--	--
26. $Co(n\text{-}MePz)_4(SCN)_2$	--	--	--
27. $Zn(4\text{-}MePy)_4(SCN)_2$	--	--	--
28. $Mn(2Me,5Et\ Py)_4(SCN)_2$	--	--	--
29. $Ni(4\text{-}MePy)_4(Ft)_2$	--	--	--
30. $Cd(4\text{-}MePy)_4(Ft)_2$	--	--	--
31. $Co(4\text{-}MePy)_4(Ft)_2$	--	--	--
32. $Mn(4\text{-}MePy)_4(Ft)_2$	--	--	--
33. $Mn(4\text{-}MePy)_4Cl_2$	--	--	--
34. $Ni(4\text{-}MePd)_4(SCN)_2$	--	--	--
35. $Ni(2,6\ DiMe\ Pd)_4(SCN)_2$	--	--	--
36. $Ni(N\text{-}iso\text{-}Pr\ Bz)_4(SCN)_2$	--	--	--
37. $Ni(N,N\ DiMe\text{-}p\text{-}Tn)_4(SCN)_2$	--	--	--
38. $Co(N,N\ DiMe\text{-}p\text{-}Tn)_4(SCN)_2$	--	--	--
39. $Fe(4\text{-}MePy)_4(SCN)_2$	--	--	--
40. $Fe(2Me,5Et\ Py)_4(SCN)_2$	--	--	--

close boiling points, a mixture of these two terpenes was worthtrying for separation. Nine complexes were studied for the clathration of a mixture having beta-pinene and delta-3-carene in almost equal amount. The results are shown in Table 4. The procedure and conditions of the clathration are exactly the same as described in the basic method. Seven complexes showed fair selective clathrating ability for delta-3-carene by increasing the delta-3-carene content up to 11 % from the feed to the clathrate.

Summing up the work of Part I through Part IV, eighty-eight complexes were tried for the separation of three different feed mixtures by clathration. In forty-six cases, clathration took place and the analysis of the clathrated terpenes indicated that some complexes had fair selective clathrating ability for delta-3-carene or dipentene depending upon other constituents present in the feed. So, it was thought worthtrying to improve these results by changing certain variables, selecting a few complexes from the previous parts. In the following parts, an attempt is made to find out any possible effect of these variables on the composition of the clathrated terpenes.

Table 4. Initial Investigation on Clathration

	Weight % of	
	Beta-pinene	Delta-3-carene
Feed	50.0	50.0
Complex	In clathrated terpenes	
1. $Ni(4\text{-}MePy)_4(SCN)_2$	46.3	53.7
2. $Ni(3\text{-}MePy)_4(SCN)_2$	38.4	61.5
3. $Ni(4\text{-}MePy)_2(SCN)_2$	40.8	59.2
4. $Ni(n\text{-}Hx)_4(SCN)_2$	44.6	55.4
5. $Ni(3,4\ Ln)_4(SCN)_2$	45.9	54.1
6. $Ni(n\text{-}MePz)_4(SCN)_2$	45.7	54.3
7. $Ni(Pl)_4(SCN)_2$	45.7	54.3
8. $Ni(Py)_4(SCN)_2$	--	--
9. $Ni(2Me,5Et\ Py)_4(SCN)_2$	--	--

Part V :

The purpose of this part was to study the effect of varying the feed size, that is, changing the feed to complex ratio, on the composition of the clathrated terpenes. The amount of the complex taken was 0.1 gm-mole and it was held constant in all cases. Nickel (4-methylpyridine)$_2$(thiocyanate)$_2$ was selected as a representative complex because it had shown some selectivity towards delta-3-carene. The feed mixture consisted of alpha-pinene, beta-pinene and delta-3-carene each in equal proportions for these tests. Results are tabulated in Table 5. It is easy to conclude that the feed/complex ratio has virtually no effect on the composition of the clathrated terpenes. This may apply to other complexes also.

Part VI :

In this part, the temperature at which clathration takes place was changed to see its effect on the composition of the clathrated terpenes. Several complexes selected from Part II were tried with a feed containing alpha-pinene, beta-pinene and delta-3-carene each in equal proportions at three different temperatures other than room temperature. Table 6 shows all the complexes tried at different temperatures along with the composition of the clathrated terpenes.

Table 5. Effect of Feed/Complex Ratio on the Clathrate Composition

Complex : $Ni(4\text{-}MePy)_2(SCN)_2$, 36.1 gms., 0.1 gm-mole

Feed Size, mls.	Feed / Complex Weight Ratio	Weight % of Alpha-pinene	Weight % of Beta-pinene	Weight % of Delta-3-carene
Feed		33.3	33.3	33.3
		In clathrated terpenes		
1. 20	0.542	30.8	30.8	38.3
2. 40	1.084	33.4	30.0	36.6
3. 60	1.626	31.2	31.0	37.8
4. 80	2.168	29.5	32.3	37.2
5. 100	2.710	32.6	30.6	36.6

Table 6. Effect of Temperature on the Clathrate Composition

	Temp, °C	Weight % of Alpha-pinene	Weight % of Beta-pinene	Weight % of Delta-3-carene
Feed		33.3	33.3	33.3
Complex		In clathrated terpenes		
1. $Ni(4\text{-}MePy)_2(SCN)_2$	84	24.6	30.8	44.7
	25*	32.5	29.9	37.6
	5	31.6	32.6	35.6
2. $Ni(4\text{-}MePy)_4(SCN)_2$	25*	31.4	31.7	37.0
	5	32.5	30.9	36.6
3. $Co(3,4\ Ln)_4(SCN)_2$	25*	32.1	30.7	37.2
	5	33.8	28.8	37.4
4. $Ni(n\text{-}Hx)_4(SCN)_2$	25*	32.2	29.2	38.5
	5	33.1	24.7	42.7
	-6	31.8	30.2	37.1

* This refers to room temperature and results from Table 2.

A comparison of the compositions of clathrated terpenes, when different temperatures are employed for the clathration, indicates that temperature has some effect but not a significant influence on the composition of the clathrated terpenes. A moderate change in temperature does not change the selective clathrating ability of a complex radically.

Part VII :

The objective of this part was to study any possible effect of varying the feed composition on the composition of the clathrated terpenes. Two complexes, nickel(n-hexylamine)$_4$(thiocyanate)$_2$ and nickel(4-methylpyridine)$_2$(thiocyanate)$_2$ were selected because they had shown better results than other complexes in Part VI. These complexes were tried at 5 °C and the ratio of complex to feed was kept constant as given in the basic method.

Table 7 shows all the different feed compositions tried and the compositions of the clathrated terpenes. In conclusion, it can be said that under the conditions of the clathration employed and for the complexes studied, the feed composition did not have any remarkable influence on the selective clathrating abilities of the complexes.

Table 7. Effect of Feed Composition on the Clathrate Composition

	Approximate weight % of			Weight % of		
	Alpha-pinene	Beta-pinene	Delta-3-carene	Alpha-pinene	Beta-pinene	Delta-3-carene
	In feed			In clathrated terpenes		
			$Ni(n\text{-}Hx)_4(SCN)_2$ at 5 °C			
1.	40.0	40.0	20.0	41.4	32.8	25.8
2.	33.3	33.3	33.3	33.1	24.7	42.7
3.	30.0	30.0	40.0	29.9	26.0	44.1
4.	20.0	20.0	60.0	19.0	16.1	64.9
5.	10.0	10.0	80.0	10.0	9.2	80.8
			$Ni(4\text{-}MePy)_2(SCN)_2$ at 5 °C			
1.	40.0	40.0	20.0	37.8	40.0	22.2
2.	33.3	33.3	33.3	31.6	32.6	35.6
3.	30.0	30.0	40.0	24.7	25.8	49.4

Part VIII :

At this stage, the column of 10 ft. length was replaced by a new column of 15 ft. length in the gas chromatograph to verify the results obtained on the previous column. For this purpose, nickel(4-methylpyridine)$_2$(thiocyanate)$_2$ complex was studied again with three different feed compositions. When the clathrated terpene mixture was analyzed with the new column, a peak of an unidentified compound, in addition to the peaks of n-pentane, alpha-pinene, beta-pinene and delta-3-carene, appeared on the chart paper in each case. All the results are tabulated in Table 8 and from this Table it is clear that the unidentified compound (designated by X) is present in a significant amount in the clathrated terpenes.

It was necessary to identify this compound, as its proportion in the clathrated terpenes was significantly large. Two different methods were employed for its identification as described in the following part.

Part IX :

One method involves the use of a gas chromatograph to identify a substance in a mixture. For this purpose, a small amount of the mixture is taken and a very small amount

Table 8. Effect of Feed Composition on the Clathrate Composition

Complex : Ni(4-MePy)$_2$(SCN)$_2$, 0.1 gm-mole, at 5 °C

Feed size : Approximately 50 mls.

Run	Constituent	Weight % in feed	Weight % in clathrated terpenes
1.	Alpha-pinene	40.0	36.5
	Beta-pinene	40.0	39.4
	Delta-3-carene	20.0	21.3
	X	--	2.8
2.	Alpha-pinene	30.0	14.9
	Beta-pinene	30.0	5.5
	Delta-3-carene	40.0	18.5
	X	--	61.0
3.	Alpha-pinene	20.0	10.0
	Beta-pinene	20.0	9.8
	Delta-3-carene	60.0	39.0
	X	--	41.0

X : Unidentified compound

of a known pure compound, which might be guessed for the unidentified compound, is added to the mixture. The resultant mixture is analyzed on the gas chromatograph and if the guess is right, an increase in the peakarea of the unidentified compound will be observed. However, the converse of this statement is not always true. If the unidentified compound and the known compound happen to have their retention times very close, then instead of two separate peaks, one bigger peak may appear on the chart paper. Therefore, other independent method must be employed in addition to this method for the identification purpose.

In the present investigation, the unidentified compound was suspected to be one of the monoterpene hydrocarbons. So six terpenes and also 4-methylpyridine were tried for the identification by the gas chromatograph method. They were:

(1) p-cymene
(2) Dipentene
(3) Alpha-terpinene
(4) Gamma-terpinene
(5) Myrcene
(6) Alpha-phellandrene
(7) 4-Methylpyridine

The unidentified compound seemed to be myrcene. However, as mentioned earlier, this may not guarantee an absolute identification. So infra-red spectroscopy was also employed for the identification.

Infra-red spectroscopy involves the passing of infra-red rays through a compound and recording the absorption or transmittance of the compound for all the wavelengths encountered in infra-red rays. Much of infra-red work depends on associating a particular frequency with a characteristic group or structural unit and noting also the maximum intensities of the corresponding absorption band. These points lead into the topic of qualitative analysis and structural problems. One way to identify a compound is to examine it by infra-red spectrometer and compare its result with that of a known compound which might be guessed for the unidentified compound. If both the results are quite similar, the unidentified compound is the known compound used for its identification.

To use this method, it was necessary to obtain the unidentified compound in the pure form from the mixture. This unidentified compound was separated from the mixture using the gas chromatograph as described in the following paragraphs.

Firstly, the clathrated terpenes (extracted with n-pentane) were warmed to evaporate most of n-pentane. By doing this, the proportion of the terpenes in the mixture was increased.

About 10 microliters of this mixture were injected into the gas chromatograph instrument. When the peak of the unidentified compound started to appear on the chart paper, a U-tube of glass, kept in a dry ice-acetone bath, was connected to the gas outlet of the gas chromatograph. The gas coming out at this time contained the unidentified compound along with the carrier gas hydrogen. The unidentified compound was condensed in the U-tube. This was repeated about 15 times, so that the amount of the unidentified compound was about one or two drops, sufficient for infra-red spectroscopic test. This unidentified compound was then examined on an infra-red spectrometer. The plot of % absorption vs. wavelength obtained for the unidentified compound was compared with that of pure myrcene available from literature.[6] (see Figure 1 and 2) The comparison indicated that both the plots showed exactly the same absorption bands at corresponding frequencies. This confirmed the identification done on the gas chromatograph. Thus, two independent methods indicated that the unidentified compound was myrcene.

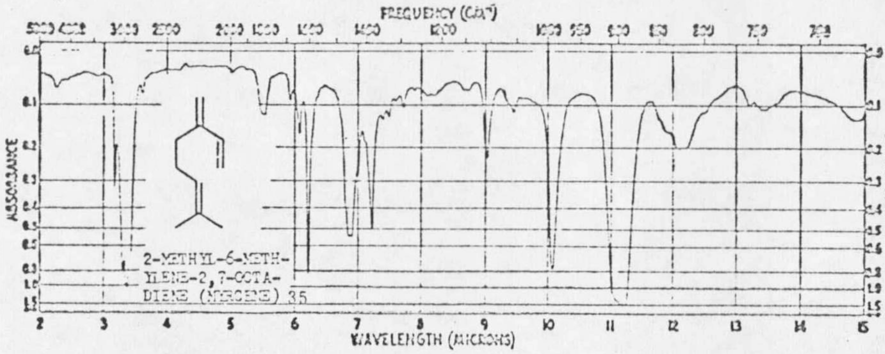

Figure 1. Infra-red Spectra of Myrcene Available in Literature. (6)

Figure 2. Infra-red Spectra of Myrcene
Obtained in this Investigation.

Part X :

When nickel(4-methylpyridine)$_2$(thiocyanate)$_2$ complex was tried for the clathration with a feed consisting of alpha-pinene, beta-pinene and delta-3-carene, the clathrated terpenes contained myrcene in a significant proportion. So, it was worthtrying to standardize the conditions under which myrcene was obtained in the clathrated terpenes.

The complex to feed ratio was kept the same as in Part VIII (shown in Table 8) and the clathration was carried out at 5 °C. Twelve runs were made with these conditions and the clathrate was air-dried, applying vacuum, for different lengths of time.

Table 9 shows the compositions of the clathrated terpenes along with the hours of drying. The proportion of myrcene goes on increasing with an increase in the duration of drying, up to a certain point. This may be explained in the following way.

At the start of drying, there are some unclathrated terpenes on the surface of a clathrate which may be a result of sticking or absorption. If the clathrate is broken at this stage, the composition of the clathrated terpenes may

Table 9. Standardization of Conditions for Obtaining Myrcene in the Clathrate

Complex : $Ni(4\text{-}MePy)_2(SCN)_2$, 0.1 gm-mole, at 5 °C

Feed size : Approximately 50 mls.

Run	Hours of drying	Weight % of			
		Alpha-pinene	Beta-pinene	Delta-3-carene	Myrcene
	Feed	33.3	33.3	33.3	--
		In clathrated terpenes			
1.	1	38.0	31.0	31.0	Tr*
2.	3	37.2	26.9	35.9	Tr*
3.	4	32.2	25.5	38.0	4.2
4.	4½	28.7	25.0	39.8	6.4
5.	14½	24.5	3.0	55.8	16.6
6.	16½	2.0	0.0	47.6	50.4
7.	22	6.4	0.0	29.7	64.0
8.	24	21.1	19.0	26.0	33.8
9.	36	28.9	8.6	20.3	42.1
10.	36	31.1	4.7	21.0	43.2
11.	50	25.3	23.4	27.0	24.4
12.	60	31.3	11.9	19.6	37.1

* Tr means % of myrcene was less than 2.0

not be regarded as the composition of truly (or solely) clathrated terpenes. The composition of this truly clathrated terpenes can be obtained if the clathrate is broken after complete removal of unclathrated terpenes by drying. It is apparent that myrcene is selectively clathrated, but its proportion in first four runs is small compared to subsequent runs because of incomplete drying. However, further work is desirable to determine the effect of other variables on the composition of the clathrated terpenes.

It is concluded that to obtain myrcene in a significant proportion in the clathrated terpenes, the following conditions are suitable.

(1) Clathrating agent: Nickel(4-methylpyridine)$_2$(thiocyanate)$_2$, 0.1 gm-mole.

(2) Feed size: Approximately 50 mls.

(3) Clathration temperature: 5 °C.

(4) Drying of the clathrate, at least for 16 hours, following filtration.

Part XI :

Since the proportion of myrcene in the clathrated terpenes was quite large, it was essential to find out the possible sources of myrcene.

Two possible sources, which might be thought of, are:

(1) Myrcene may be present in the feed* as an impurity and is concentrated during the clathration.

(2) There may be a reaction from beta-pinene to myrcene along with the clathration.

To check the first possibility, each of the feed constituents was analyzed separately on the gas chromatograph. The results indicated that alpha-pinene and delta-3-carene did not contain myrcene but beta-pinene contained some myrcene. The complete analysis of beta-pinene was:

alpha-pinene	1.37	weight %
myrcene	6.25	weight %
beta-pinene	92.4	weight %

Since the amount of the clathrated terpenes was usually very small (less than 5 mls.), it was considered possible that myrcene was concentrated during the clathration. One more run was made to check this possibility. A feed of alpha-pinene, beta-pinene and delta-3-carene, each taken in equal proportion,

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* The composition of the feed reported in most Tables is based on the proportion of each constituent mixed to prepare the feed and the impurities associated with the constituents are not taken into account.

was clathrated as described in Part X. Obviously, 50 mls. of this feed contained approximately 1.08 mls. of myrcene. The analysis of the clathrated terpenes was:

alpha-pinene	24.0	weight %
beta-pinene	20.3	weight %
delta-3-carene	34.7	weight %
myrcene	21.0	weight %

The volume of the clathrated terpenes was about 4.7 mls. and it would contain about 0.987 mls. of myrcene. Considering the material balance of myrcene, it could be said with reasonable confidence that almost all myrcene was clathrated and that myrcene was not generated by a reaction during the clathration. The following two tests supported this idea.

(1) The unclathrated terpenes, coming out along with the filtrate, were analyzed on the gas chromatograph. The result was:

alpha-pinene	33.4	weight %
beta-pinene	32.3	weight %
delta-3-carene	34.3	weight %

It did not contain myrcene at all and its composition was very near to that of feed. This was an indication that all myrcene was clathrated.

(2) To find out whether or not there was a reaction from beta-pinene to myrcene, it was desirable to clathrate beta-pinene not containing myrcene. For this purpose, myrcene was removed from beta-pinene as described in the following paragraph.

Maleic anhydride was dissolved in acetone and beta-pinene added into it and allowed with stirring for about 24 hours for completion of a reaction between myrcene and maleic anhydride. The reaction product was soluble in a sodium hydroxide solution. A solution of sodium hydroxide was added into the reaction product to separate out beta-pinene as a hydrocarbon phase. Beta-pinene was then washed three times with the sodium hydroxide solution and finally warmed for about 15 minutes to evaporate small amount of acetone.(8) Its analysis indicated that it did not contain myrcene at all, although it did contain some alpha-pinene as before.

This beta-pinene, free of myrcene, was clathrated as indicated in the previous part and the analysis of the clathrated terpenes showed that there was no myrcene at all. Therefore, it was concluded that there was no reaction from beta-pinene to myrcene during the clathration.

From the results of this part, it was concluded that nickel(4-methylpyridine)$_2$(thiocyanate)$_2$ showed a remarkable selective clathrating ability for myrcene.

Part XII :

Since it was beta-pinene only which contained myrcene, further work was done on the clathration of beta-pinene containing myrcene. The purpose of this part was to study the effect of varying the feed to complex ratio and varying the proportion of myrcene in the feed, on the composition of the clathrated terpenes.

Table 10 shows the different feed sizes of beta-pinene tried for the clathration with 0.1 gm-mole (constant for all tests) of the complex and the compositions of the clathrated terpenes. It is clear that the feed size of 90 mls. is most suitable for selective clathrating of myrcene. However, for a different feed composition this may not be the most suitable size for the selective clathration.

Figure 3 shows the graphical representation of the results of Table 10. From this plot, it is clear that maximum concentration of myrcene in the clathrated terpenes can be obtained when the feed to complex weight ratio is in the

Table 10. Effect of Feed/Complex Ratio on the Proportion of Myrcene in the Clathrate

Complex : $Ni(4\text{-}MePy)_2(SCN)_2$, 36.1 gms., 0.1 gm-mole

	:Feed:		Feed/Complex	Weight % of		
	Size, mls.	Weight, gms.	Weight ratio	Alpha-pinene	Beta-pinene	Myrcene
		Feed		1.37	92.4	6.25
				In clathrated terpenes		
1.	15	14.7	0.407	6.4	48.2	45.4
2.	30	29.4	0.814	6.65	33.3	60.0
3.	45	44.1	1.221	3.52	30.7	65.7
4.	90	88.2	2.442	0.0	28.0	72.0
5.	200	173.0	4.800	0.0	40.0	60.0

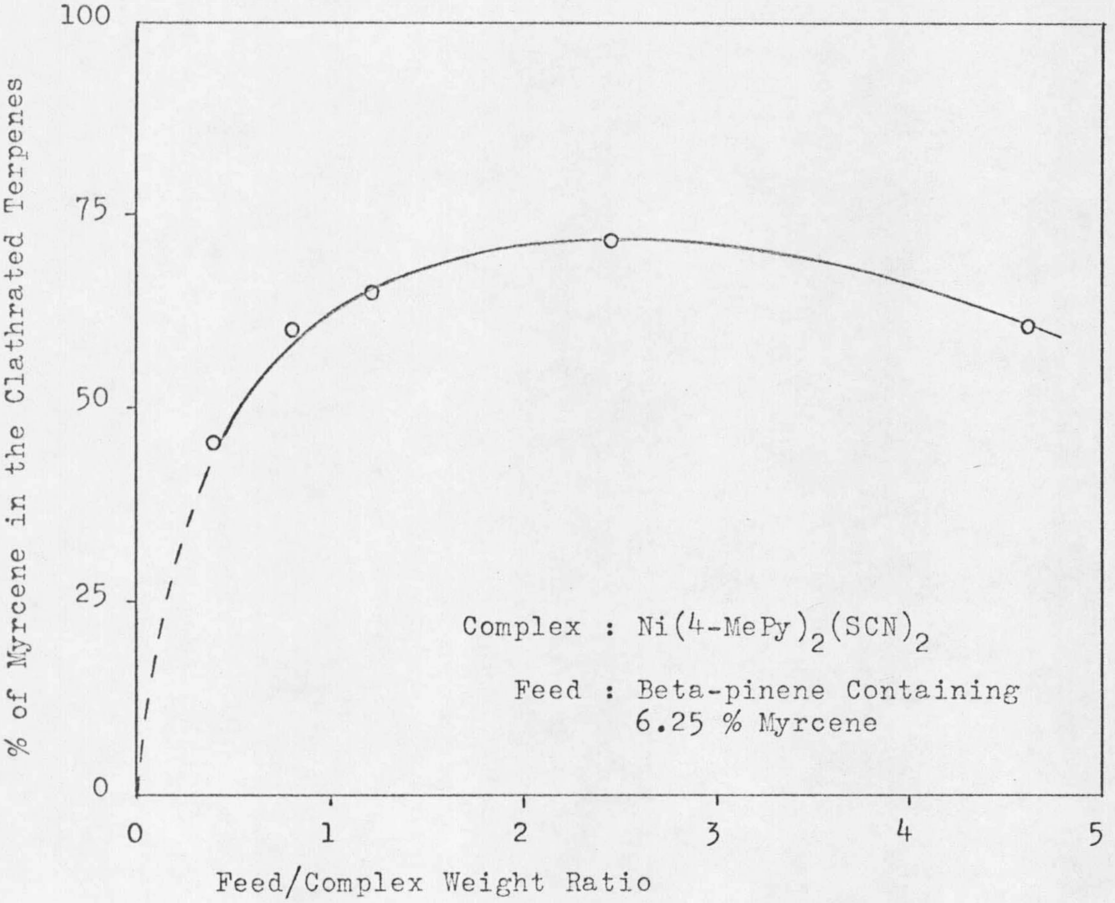

Figure 3. Effect of Feed/Complex Ratio on the Composition of the Clathrated Terpenes.

range of 2 to 3.

Table 11 shows the effect of the feed composition on the composition of the clathrated terpenes for a definite feed to complex weight ratio of 1.221. Figure 4 is the graphical representation of the same results. An increase in the proportion of myrcene in the feed results in an increase in the proportion of myrcene in the clathrated terpenes. Myrcene is concentrated from 25 % in the feed to about 90 % in the clathrated terpenes in one clathration stage.

The nature of the curve indicates that it does not pass through a point of maxima and its slope is always positive. A further increase in % of myrcene in the feed will probably extend the curve almost in a straight line to pass through the point (100,100).

It is concluded that nickel(4-methylpyridine)$_2$(thiocyanate)$_2$ has an excellent selective clathrating ability for myrcene when clathration is carried out at 5 ^{o}C and the clathrate is completely dried.

Table 11. Effect of Varying Myrcene Proportion in the Feed on its Proportion in the Clathrate

Complex : Ni(4-MePy)$_2$(SCN)$_2$, 18.05 gms., 0.05 gm-mole

Feed size : 22.5 mls.

Feed/Complex Weight Ratio : 1.221

	Approximate weight % of			Weight % of		
	Alpha-pinene	Beta-pinene	Myrcene	Alpha-pinene	Beta-pinene	Myrcene
		In feed		In clathrated terpenes		
1.	1.42	95.6	3.0	12.55	26.7	60.7
2.	1.37	92.4	6.25	3.52	30.7	65.7
3.	1.29	86.7	12.0	3.64	14.2	82.1
4.	1.2	81.3	17.5	5.44	9.6	85.0
5.	1.1	73.9	25.0	0.0	10.4	89.6

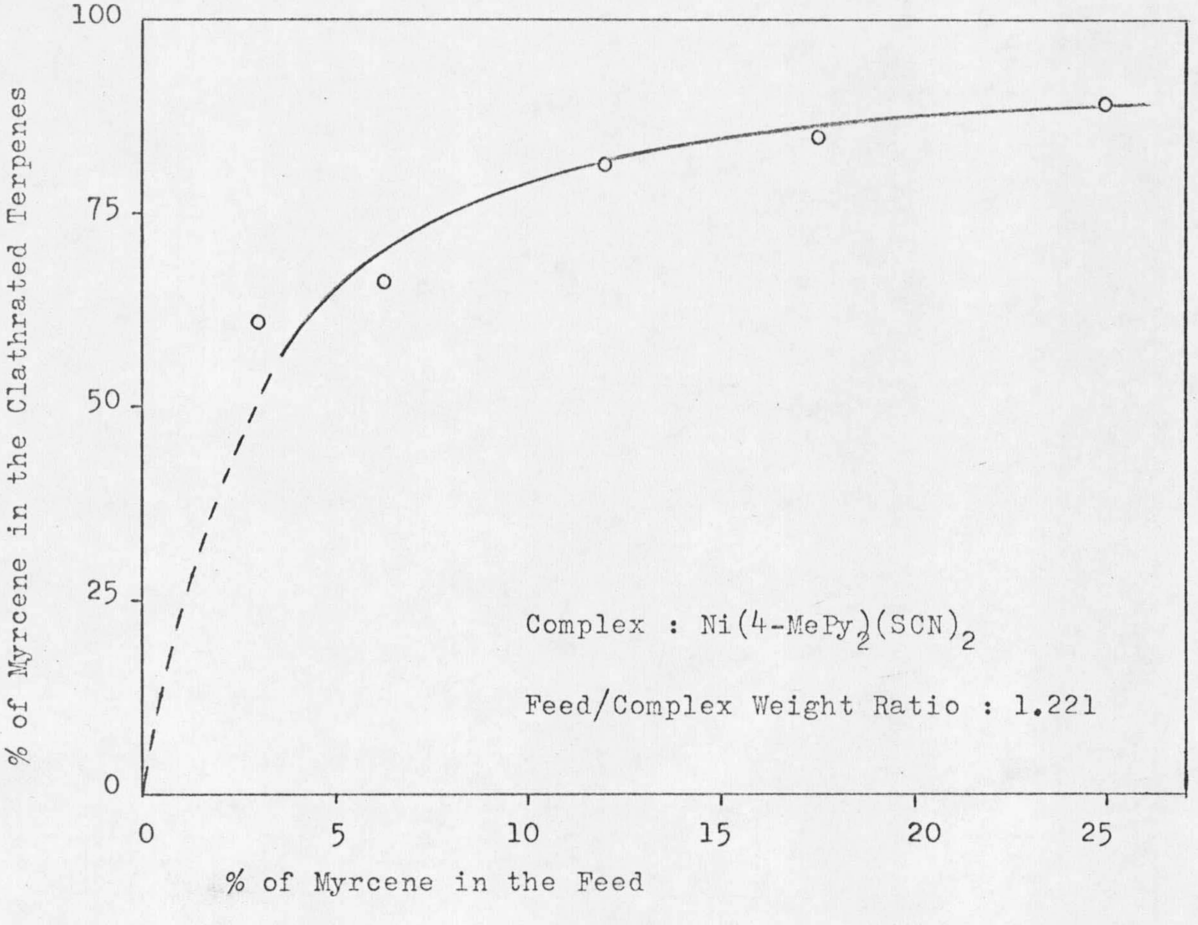

Figure 4. Effect of Feed Composition on the Composition of the Clathrated Terpenes.

CONCLUSIONS

(1) Various Werner complexes were tried for the separation of three different feed mixtures consisting of alpha-pinene, beta-pinene, delta-3-carene and dipentene. Several complexes have shown fair selective clathrating ability for delta-3-carene and dipentene as indicated by a 5 to 10 % increase in the concentration of these constituents.

(2) Several variables such as clathration temperature, feed to complex weight ratio, feed composition etc. did not have a significant influence on the compositions of the clathrated terpenes for most of the clathrating agents studied.

(3) The above two conclusions do not apply to a rather exceptional complex viz. nickel(4-methylpyridine)$_2$(thiocyanate)$_2$. This complex exhibited an excellent selective clathrating ability for myrcene, which was present as an impurity in beta-pinene. In a single clathration stage, this complex concentrated myrcene from 2 % in the feed to 61 % in the clathrated terpenes. For this particular clathrating agent, feed to complex weight ratio and feed composition had a remarkable influence on the composition of the clathrated terpenes. An increase in the feed to complex weight ratio increased the proportion of myrcene in the clathrated terpenes, up to a certain limit. Also, an increase in the proportion of myrcene

increased its proportion in the clathrate. Myrcene was concentrated from 25 % in the feed to about 90 % in the clathrate, in one clathration stage.

(4) Boiling points of beta-pinene (164-6 °C) and myrcene (167 °C) are very close and therefore, difficult to separate by fractional distillation. It is apparent that they can be separated by the clathration technique.

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