MORPHOLINE AS A SELECTIVE SOLVENT FOR REFINING
LUBRICATING OIL

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LUBRICATING OIL

By

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Bachelor of Science

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Stillwater, Oklahoma

1937

Submitted to the Department of Chemical Engineering

Oklahoma Agricultural and Mechanical College

In Partial Fulfillment of the Requirements

For the degree of

MASTER OF SCIENCE

1939

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ACKNOWLEDGMENT

The author wishes to acknowledge the constructive criticism and generous advice given by Dr. Charles L. Nickolls, under whose direction this work has been carried out, and by Dr. Otis C. Dermer. The author wishes further to acknowledge the facilities provided for this research by the Chemical Engineering Department of the Oklahoma Agricultural and Mechanical College.

PREFACE

Lubricating oils are manufactured from petroleum stocks which are generally classified in the United States as Pennsylvania, Mid-Continent, and Coastal. These classes show marked differences in physical properties and lubricating characteristics and require various degrees of refining. The Coastal crudes require the most severe treatment, Pennsylvania the least, and Mid-Continent oils occupy an intermediate position.

In the past, almost all of the chemical refining has been done with sulfuric acid; recently, however, extraction with solvents has found important commercial application. Among the advantages claimed for solvent extraction are:

1. Production of a better grade of lubricant.
2. Elimination of the problem of acid sludge disposal.
3. Utilization of the extract portion as a by-product or as cracking stock.
4. Production of a higher yield.

On the basis of the cost of production per barrel of oil, solvent extraction is more economical than the acid treating process. For these reasons, it seems quite probable that solvent refining will soon supplant the older process, at least in the Mid-Continent area.

There are many solvents now in commercial use, the choice of a specific one depending on the stock to be treated and the comparative cost of the process. There are, however, many solvents as yet untried even in the laboratory, and it

is the purpose of this thesis to present data for one of
the newer aliphatic amines, morpholine.

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INTRODUCTION

Because of the great number and complexity of the hydro-
carbons in petroleum, it is impossible to determine strictly
theoretical conditions for solvent extraction of a lubri-
cating oil stock. In order to simplify computations, stocks
may be considered to be a mixture of "naphthenes" and
"paraffins" (10).

As an index of the degree of naphthenicity, several
physical constants have been suggested. Most generally used
for correlation of solvent extraction data are the viscosity-
gravity constant proposed by Hill and Coats (9), and the
viscosity index of Dean and Davis (4). McCluer and Fenske
have shown the relationship between these two with data on
58 samples (13). Mikeska (14) has made a study of the
correlation of viscosity-gravity constant, viscosity index,
refractive index, and other physical properties with the
chemical composition of some of the compounds found in
petroleum.

The so-called naphthenic constituents are those which
consist of hydrocarbons relatively poor in hydrogen and
which have a high value of the viscosity-gravity constant
and a low viscosity index. The paraffinic constituents are
relatively rich in hydrogen, have a low viscosity-gravity
constant, and a high viscosity index.

A good lubricating oil should have a low viscosity-
gravity constant, a high viscosity index, a low pour point,
a low carbon residue, and be resistant to oxidation (21).
Lowering the pour point depends upon the degree of wax

removal which is in itself a separate problem. However, the pour point may be altered by solvent extraction of the type with which this thesis deals. Since high viscosity-gravity constants, low viscosity indices, and low resistance to oxidation are characteristics of the naphthenic constituents, it is necessary to remove these components by suitable refining methods.

The first commercial application of solvent extraction of petroleum fractions was the Edeleanu process for refining kerosene with liquid sulfur dioxide (6). For extraction of the more viscous petroleum stocks, liquid SO_2 is diluted with other solvents such as benzene and acetone. Since the investigation of 110 solvents by Ferris, Birkhimer, and Henderson (8) the application of solvent extraction has increased very rapidly. Other investigators have reported varying degrees of success with numerous solvents, and there is quite a number now in commercial use. Among these may be mentioned nitrobenzene, furfural, Chlorex, Duo-Sol, phenol, crotonaldehyde, and propane (16).

The procedure in solvent extraction is as follows: solvent and stock are mixed thoroughly in a given ratio and allowed to separate at a predetermined temperature into two phases. The solvent is then reclaimed from each fraction.

Solvents for refining lubricating oil stocks may be one of two types: (a) those which dissolve the undesirable portions and have little effect on the paraffinic constituents, and (b) those which dissolve the desirables and not the naphthenes. According to Kyropoulos (12), the separa-

tion of petroleum stocks into two fractions by polar
solvents is due to the formation of dipole association
complexes, the solvent forming more stable compounds with
the undesirable constituents and therefore extracting them.
Solvents of type (b) are non-polar and so dissolve those
hydrocarbons which do not form dipole compounds. Extrac-
ting processes may involve the use of either or both of
these two types. Examples of the first type of solvents
are nitrobenzene, phenol, Chlorex, and furfural; an example
of type (b) is propane; and the Duo-Sol process is a method
using both types.

Selectivity is the term applied to the ability of a
solvent to dissolve certain constituents to the exclusion
of others, and it is necessary that a solvent have a
"high" selectivity. Since the most economical separation
into two phases depends upon the action of gravity, a
solvent must have a density widely different from that of
the oil to be treated. Since the solvent must generally be
reclaimed by distillation, low boiling point and stability
to heat are advantageous. It is obvious that the solvent
must be available in commercial quantities. Toxicity and
corrosivity should also be considered. Ferris, Birkhimer,
and Henderson (8) and Kyropoulos (12) conclude that the
selectivity of a solvent depends upon its structure. A
cyclic structure and the presence of a polar group are
desired, but the presence of an aliphatic side chain on
the ring decreases the selectivity. Morpholine has the
semi-structural formula. $O \overset{(CH_2)_2}{\underset{(CH_2)_2}{\diagup\diagdown}} NH$
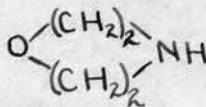
From the conclusions given above it can be predicted that morpholine should have a high selectivity.

There are four general methods by which a solvent extraction may be carried out:

(1)　Single stage batch extraction

(2)　Multiple extraction (n stages)

(3)　Batch counter-current extraction (n stages)

(4)　Counter-current extraction in a packed tower.
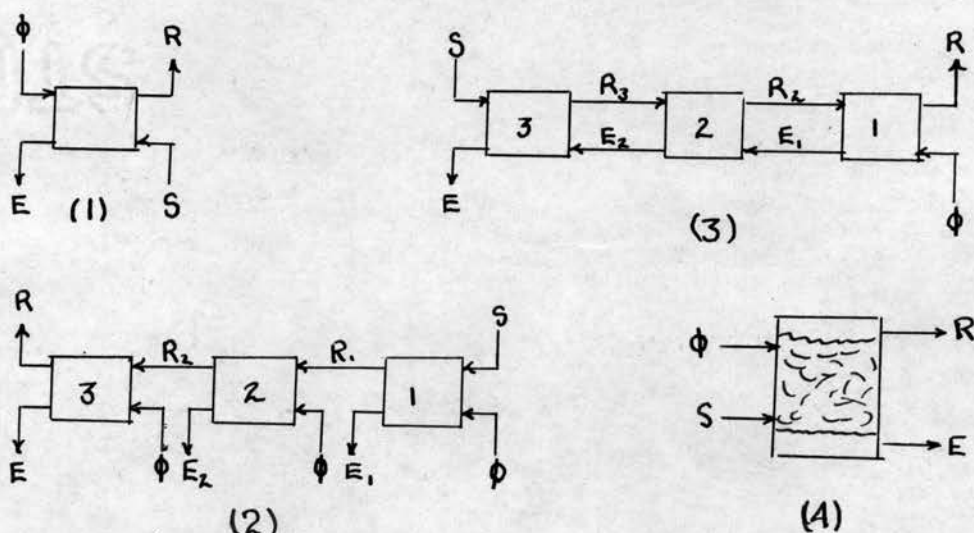
In these schematic diagrams, ϕ represents solvent, S represents stock to be treated, and R and E represent raffinate and extract, respectively.

In the past all four of these systems have been used commercially, but the trend has been toward adoption of the latter two.　Varteressian and Fenske (18) point out that cost data and the grade of oil which is desired determine which of these methods may be most advantageously employed.

Granting that the number of theoretical stages is constant, the process variables for a given stock are

temperature and solvent ratio. The main purpose of correlating laboratory data is to predict values for the final conditions in a solvent extraction when values of these two variables are given.

To correlate data on solvent extraction, the system of Hunter and Nash (10, 7) using ternary diagrams has been adopted. Kurtz suggests the use of rectangular coordinates (11).

Owing to our incomplete state of knowledge as to the exact chemical composition of petroleum and its products, extraction data must be correlated by empirical methods. The stock is split into two fractions which differ widely in physical properties; if we consider oil to be made up of varying percentages of two components with given values of physical constants, the oil-solvent mixtures can then be treated as a simple ternary system.

When the system is at equilibrium, it is necessary to record the following information in order to represent it:

    (a)   Amounts of the two phases in equilibrium

    (b)   Amount of solvent in each phase at equilibrium

    (c)   A physical property (such as viscosity-gravity constant) of the solvent-free oil present in each phase at equilibrium.

If one vertex of the triangle represents pure solvent and one side is scaled into units of the required physical property of the solvent-free oil, (b) and (c) determine coordinates for two points on a curve, one for each phase, and the connecting tie line represents (a).

If the above data are obtained for a series of single-stage extractions with varied solvent ratios, care being taken that equilibrium is attained, a binodial curve may be plotted. If the physical properties of the stock and of the refined oil, solvent ratio, and working conditions are known, it is possible to calculate for a countercurrent extraction the following data:

(a) The yield of refined oil and of extract.

(b) The amount of solvent in each phase.

(c) The value of the physical constant for the oil.

(d) The number of ideal extraction stages necessary in order to obtain the desired oil.

If the number of extraction stages is known, the physical constant of the refined oil can be calculated, as shown below.

Suppose for example the binodial curve KQNLPR has been determined for treatment of a stock with a viscosity-gravity constant D, and that by countercurrent extraction of n theoretical stages it is desired to obtain a raffinate oil of viscosity-gravity constant J. The intersection of JB with the curve gives the point K which represents the composition of raffinate from the final stage. By a material balance it can be shown that KML must intersect DB at M so that DM/MB equals the ratio of volume of solvent to total volume. Point L gives the composition of the extract layer which must be in equilibrium with a phase of composition, N, on the other end of the tie line for the first stage. DL and JKR are extended and point O located at their intersection. Also by material balance it can be shown that the intersection
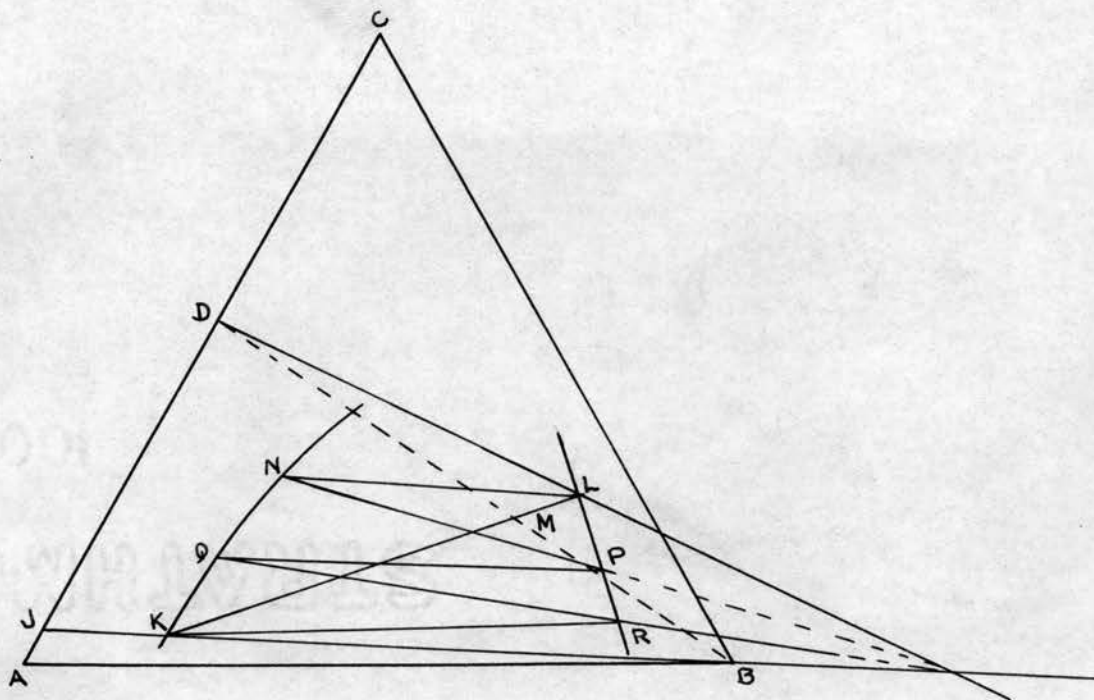
of NO with the curve gives point, P, which is the composition
of the extract layer from the second stage. Construction of
the tie line from P gives Q which denotes the raffinate
phase in equilibrium with P. Progressing in a similar
manner a point on or below K can be found and the number of
stages necessary will thus be calculated.

Where the number of stages is known and it is desired
to calculate the composition of the raffinate and extract
phases, the solution is by trial and error. A raffinate
composition is assumed and the procedure given above
followed for the given number of stages. If the calculated
and assumed raffinate compositions agree, a solution has
been obtained. If they do not, another assumption must be
made. An example of this type of calculation is shown in
Figure 4. The results for this three stage batch counter-
current extraction are given as calculated results for
Experiment 18.

EXPERIMENTAL

The "stock" oil used in these experiments was obtained from the Continental Oil Company in Ponca City, Oklahoma. It was a vacuum tower cut and was dewaxed. In their refining process, this oil is acid treated and used as a blending stock. The physical properties of this stock are given in Table I.

The solvent, morpholine, was obtained from Union Carbide and Carbon Company. It was ordinary commercial grade, having a boiling point of 126-30°C. Morpholine is a cyclic ether amine, named because of a supposed identity with the basic ring of morphine. It was discovered by Knorr in 1889, who prepared it by the action of 70% sulfuric acid upon diethanolamine. Patents have since been issued on its preparation from β,β'-diiodo-diethylether and from ethylene chlorhydrin and toluene sulfonamide (20).

Pure morpholine is colorless and has a penetrating ammoniacal odor. It absorbs moisture and CO_2 from the air. Morpholine boils at 128.9°C., freezes at -4.9°C., and its density is 0.994 (20/4° vac.) (5). It has the relatively high vapor pressure of 13 mm. at 20°C. (20).

Morpholine has been suggested as a corrosion inhibitor for water solutions, as a color stabilizer for petroleum products, as an antiknock agent for gasoline, and as a carbon remover for use on aluminum pistons (20). A patent was issued to Adams (1) covering the use of amines to improve the color of petroleum fractions.

For the single stage treatments the procedure was as

follows. Measured volumes of solvent and oil were heated with stirring to miscibility; this was done to insure equilibrium. The oil was measured in a 1000 ml. graduated cylinder, emptied into a beaker, and the adhering oil washed out with solvent, the volume of which was also measured in a 1000 ml. graduated cylinder. The solution was then placed in separatory funnels, cooled to the desired temperature, and allowed to settle for one hour. The temperature of the bath was not allowed to vary more than $0.5^{\circ}C$. The mixture separated into two phases. The upper layer consisted of "good" oil plus some solvent, and is called the raffinate; the lower layer consisted of extracted oil and the larger part of the solvent, and is called the extract. The volumes of the two phases were measured in 1000 ml. cylinders and the solvent was then distilled from each. The distillation was without vacuum up to $130^{\circ}C$. The remainder of the solvent was distilled off under vacuum. The final temperature was $145^{\circ}C$. in every case. The volume of solvent recovered was measured in graduated cylinders, the capacity of which depended on the volume to be measured. After the oil had cooled to room temperature, its volume was measured. This latter volume is not necessary for correlation but serves as a further check on removal of solvent.

The oil stock used did not begin to distill even at $190^{\circ}C$. under the vacuum used, and the solvent recovered had no color. The solvent was redistilled before being used again and the light ends discarded. This volume was usually

from 1 to 2% of the total volume redistilled and the residue left in the flask was negligible in every distillation. The oil samples were tested with moistened litmus paper to determine whether all solvent had been removed. Any morpholine which remained with the oil could also be detected by its odor.

The pseudo-countercurrent system of Watanabe and Morikawa (19) which was used by Hunter and Nash (10) and by Rushton (17) was adopted for the batch countercurrent extractions. A diagrammatic flow sheet for three stages is shown below. The procedure for each stage was essentially the same as for a single stage treatment. The mixture was heated to miscibility and then cooled in a bath.
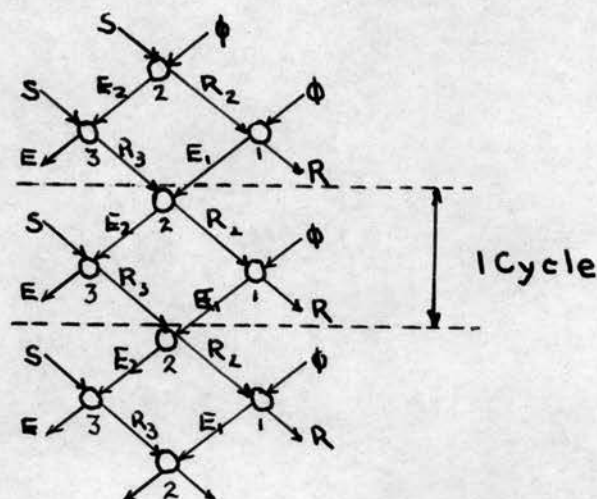
In this diagram, ϕ stands for solvent and S for oil stock. ϕ/S gives the solvent ratio. R and E represent raffinate and extract, respectively. When R and E become substantially constant in volume, the extraction is at equilibrium. This usually requires completion of three or four cycles.

For calculating the viscosity-gravity constant, the following equation is used (9):

$$V.G.C. = \frac{10\ G - 1.0752 \log (V-38)}{10 - \log (V-38)}$$

wherein G represents the specific gravity at $60^{\circ}F./60^{\circ}F.$, V represents the viscosity in Saybolt Universal seconds at $100^{\circ}F.$ The viscosity index is calculated from the viscosity in Saybolt Universal seconds at 100 and $210^{\circ}F.$ by the use of tables found in the experimental work of Dean and Davis (4). A highly paraffinic oil has a value of 0.807 for the viscosity-gravity constant and 100 or more for the viscosity index.

The viscosities were determined by the usual A.S.T.M. methods (2). For the viscous extracts the viscosity at $100^{\circ}F.$ was calculated by the use of A.S.T.M. viscosity-temperature charts. Specific gravities were calculated by the use of pycnometers, and the oil was cooled in a constant temperature bath at $60^{\circ}F.$ The Conradson carbon, flash point, and fire point were also determined using A.S. T.M. methods (3).

Table II and the accompanying curve give the data obtained for batch extraction at a settling temperature of $40^{\circ}C.$ Tables III and IV give the data for single stage extractions at 20° and $10^{\circ}C.$, respectively. Table V shows results of three stage batch-countercurrent extractions at $10^{\circ}C.$ Table VI shows values of carbon residue, flash and fire points, and color for the raffinates obtained at $10^{\circ}C.$ Table VII gives calculated and observed data for three stage extractions.

TABLE I

Physical Properties of Oil Stock

Viscosity at 100° F...................................790 sec.

Viscosity at 210° F...................................72.0 sec.

Sp. G. at 60/60° F....................................0.9075

Viscosity Index.......................................76.5

Viscosity-gravity constant............................0.840

Conradson carbon......................................0.258%

Color (Tag-Robinson)..................................0.0

Flash point...490°F.

Fire point..550°F.

TABLE II

Single Stage Extractions at 40° C.

			Volume Data					Properties of Solvent-free Oil					
Exp. No.	Solv. Ratio	Phase	Total Vol.	Vol. Oil	Vol. Solv.	%age Solv.	Visc. @ 100	Visc. @ 130	Visc. @ 210	Sp. G. @ 60/60	V.G.C.	V.I.	% Stock in Raff.
1	1:1	R	630	403	223	35.4	660	---	70.0	0.8996	0.832	90	81.0
		E	370	95	275	74.3	2425	748	101	0.9463	0.881	18	
2	1.5:1	R	535	355	180	33.3	594	---	68.0	0.8933	0.825	95	71.0
		E	715	145	570	79.7	2200	699	99	0.9443	0.879	27	
3	2:1	R	440	298	142	32.3	557	---	67.1	0.8897	0.821	99	59.8
		E	1060	201	860	81.1	1665*	560	88.3	0.9368	0.871	37	
4	3:1	R	382	257	123	32.2	510	---	65.4	0.8847	0.815	103	51.4
		E	1625	240	1380	85.0	1525	532	87.0	0.9355	0.871	43	
5	4:1	R	270	185	86	31.8	493	---	65.0	0.8795	0.808	105	46.3
		E	1730	215	1515	87.6	1502*	525	86.1	0.9356	0.871	49	

* Observed values.

Figure 1
Single Stage Extraction
at 40°C.
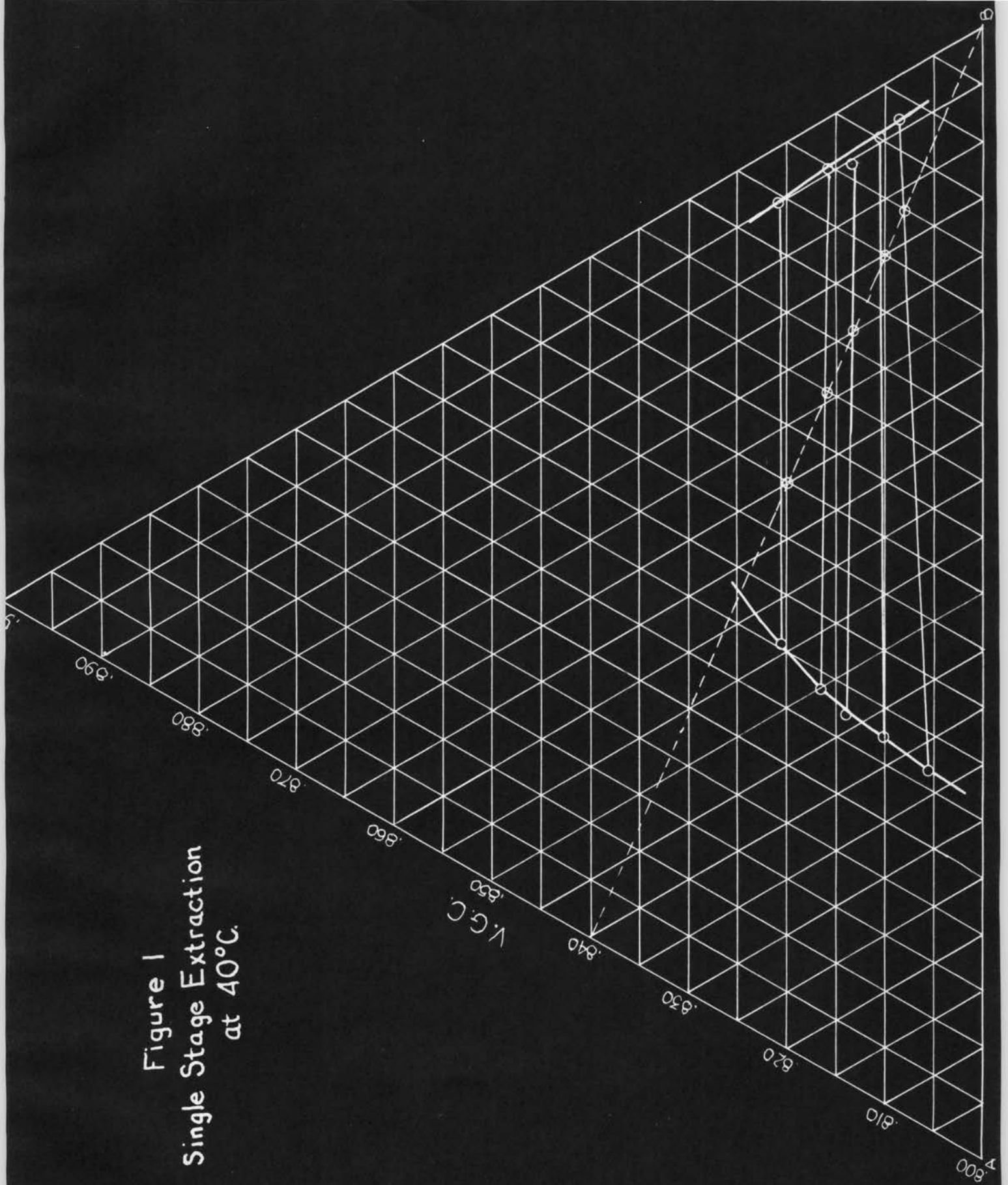
TABLE III

Single Stage Extractions at 20° C.

			Volume Data				Properties of Solvent-free Oil						
Exp. No.	Solv. Ratio	Phase	Total Vol.	Vol. Oil	Vol. Solv.	%age Solv.	Visc. @ 100	Visc. @ 130	Visc. @ 210	Sp. G. @ 60/60	V.G.C.	V.I.	% Stock in Raff.
6	0.5:1	R	1510	1175	335	22.2	679	---	70.0	0.9021	0.835	84	94.0
		E	365	75	290	79.5	9000	2197	183	0.9903	0.935	--	
7	1:1	R	823	640	182	22.1	645	---	69.7	0.8954	0.826	92	85.5
		E	677	110	565	83.4	6000	1519	145	0.9780	0.919	--	
8	2:1	R	675	525	150	22.2	565	---	67.7	0.8893	0.820	100	75.0
		E	1420	172	1245	87.7	4000	1120	126	0.9648	0.903	9	
9	3:1	R	430	335	96	22.2	511	---	65.7	0.8841	0.814	103	67.0
		E	1570	165	1400	89.1	3050	910	113	0.9541	0.889	18	
10	4:1	R	340	265	74	21.8	492	---	65.0	0.8792	0.808	105	59.0
		E	1910	185	1722	90.2	2350	742	103	0.9491	0.885	30	

Figure 2
Single Stage Extraction
at 20°C.

V.G.C
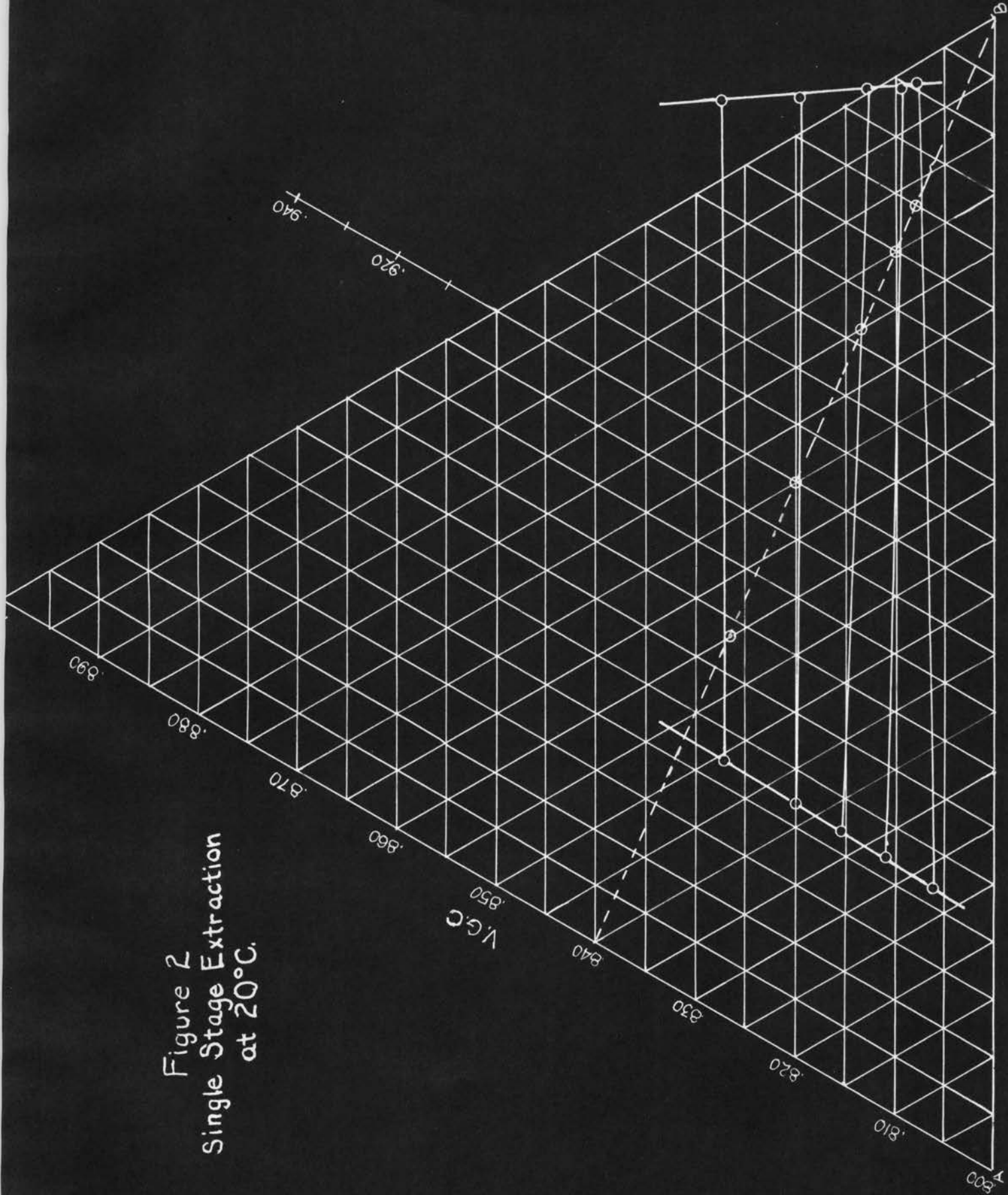
TABLE IV

Single Stage Extractions at 10° C.

			Volume Data				Properties of Solvent-free Oil						
Exp. No.	Solv. Ratio	Phase	Total Vol.	Vol. Oil	Vol. Solv.	%age Solv.	Visc. @ 100	Visc. @ 130	Visc. @ 210	Sp. G. @ 60/60	V.G.C.	V.I.	% Stock in Raff.
11	0.5:1	R	1402	1125	275	19.3	670	---	69.6	0.9014	0.834	85	95.0
		E	395	70	325	82.5	40,000	2200*	257	1.0103	0.940		
12	1:1	R	960	772	179	18.8	592	---	67.3	0.8945	0.826	93	85.9
		E	840	126	717	85.6	13,000	1670**	178	0.9933	0.935		
13	2:1	R	740	598	140	18.9	552	---	67.0	0.8883	0.819	99	80.0
		E	1510	150	1355	90.0	10,500	2220	165	0.9844	0.926		
14	3:1	R	370	300	69	18.7	532	---	66.5	0.8841	0.814	102	75.0
		E	1230	98	1130	92.0	4,800	1273	132.2	0.9769	0.920		
15	4:1	R	350	284	65	18.5	515	---	66.3	0.8800	0.809	105	71.0
		E	1650	115	1533	93.0	3,400	961	114.2	0.9725	0.916		

* Viscosity at 150°F.

** Viscosity at 140°F.

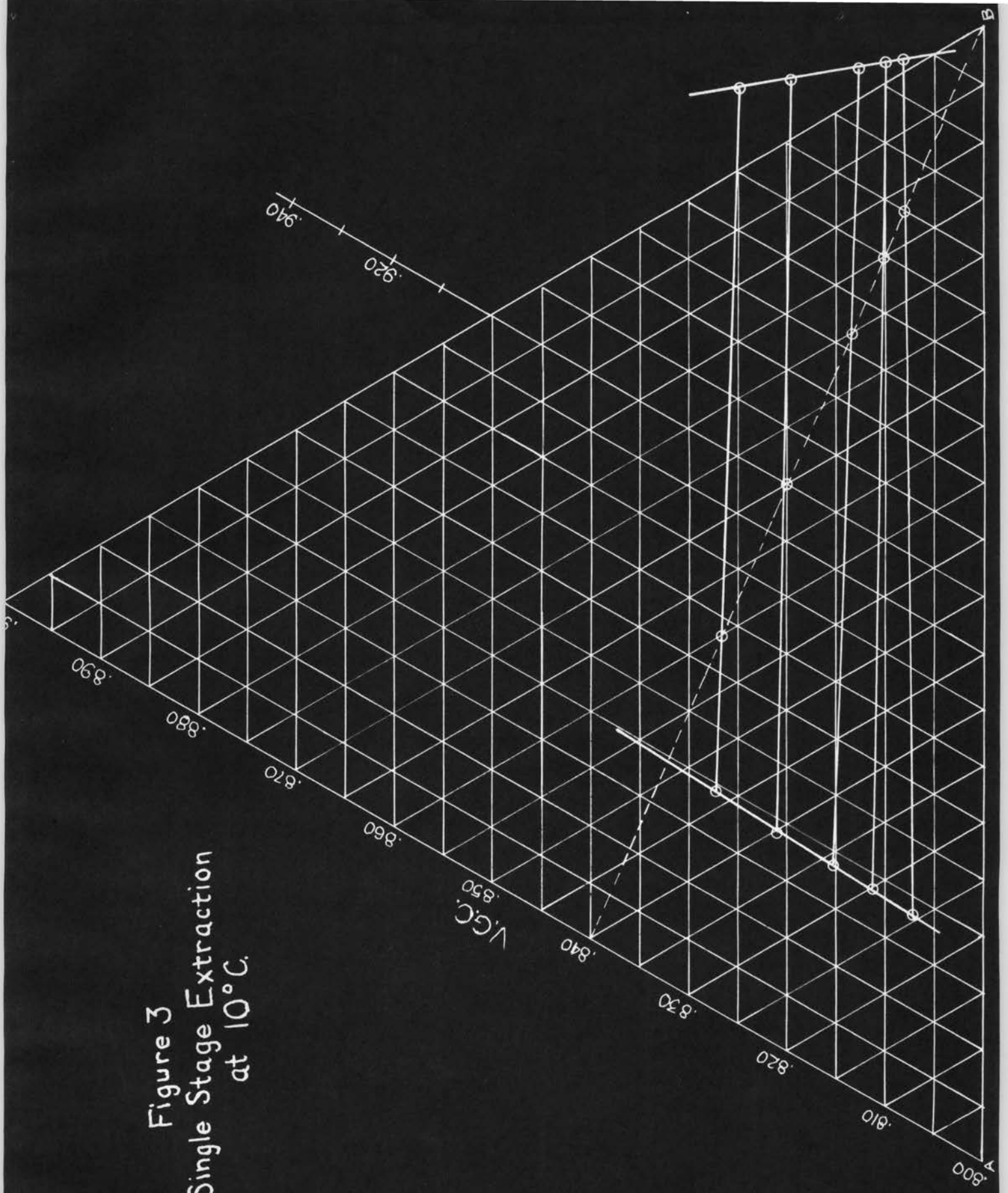Figure 3
Single Stage Extraction
at 10°C.

TABLE V

Three Stage Extraction at 10° C.

			Volume Data					Properties of Solvent-free Oil						
Exp. No.	Solv. Ratio	Phase	Total Vol.	Vol. Oil	Vol. Solv.	%age Solv.	Visc. @ 100	Visc. @ 130	Visc. @ 210	Sp. G. @ 60/60	V.G.C.	V.I.	% Stock in Raff.
16	1:1	R	498	406	90	18.1	530	---	66.5	0.8866	0.817	102	81.2
		E	502	95	407	81.4	16,500	1970*	188	0.9948	0.937		
17	1.5:1	R	470	385	85	18.1	492	---	65.0	0.8806	0.810	105	77.0
		E	170	110	660	85.7	18,500	1989	160	0.9915	0.929		
18	2:1	R	346	286	62	17.8	454	---	63.8	0.8781	0.808	109	71.5
		E	850	115	735	86.5	4,700	1256	135	0.9893	0.938		

* Viscosity at 140°F.

TABLE VI

Exp. No.	Flash Point	Fire Point	Color Tag- Robinson	V.G.C. of Raff.	Carbon Residue
11	480°F.	550°F.	1.10	0.834	0.165%
12	480°F.	545°F.	1.70	0.826	0.060%
13	475°F.	545°F.	2.70	0.819	0.038%
14	475°F.	550°F.	3.75	0.814	0.022%
15	480°F.	545°F.	2.75	0.809	0.027%
16	480°F.	545°F.	4.50	0.817	0.040%
17	475°F.	540°F.	6.50	0.810	0.002%
18	475°F.	540°F.	4.75	0.808	0.005%

TABLE VII

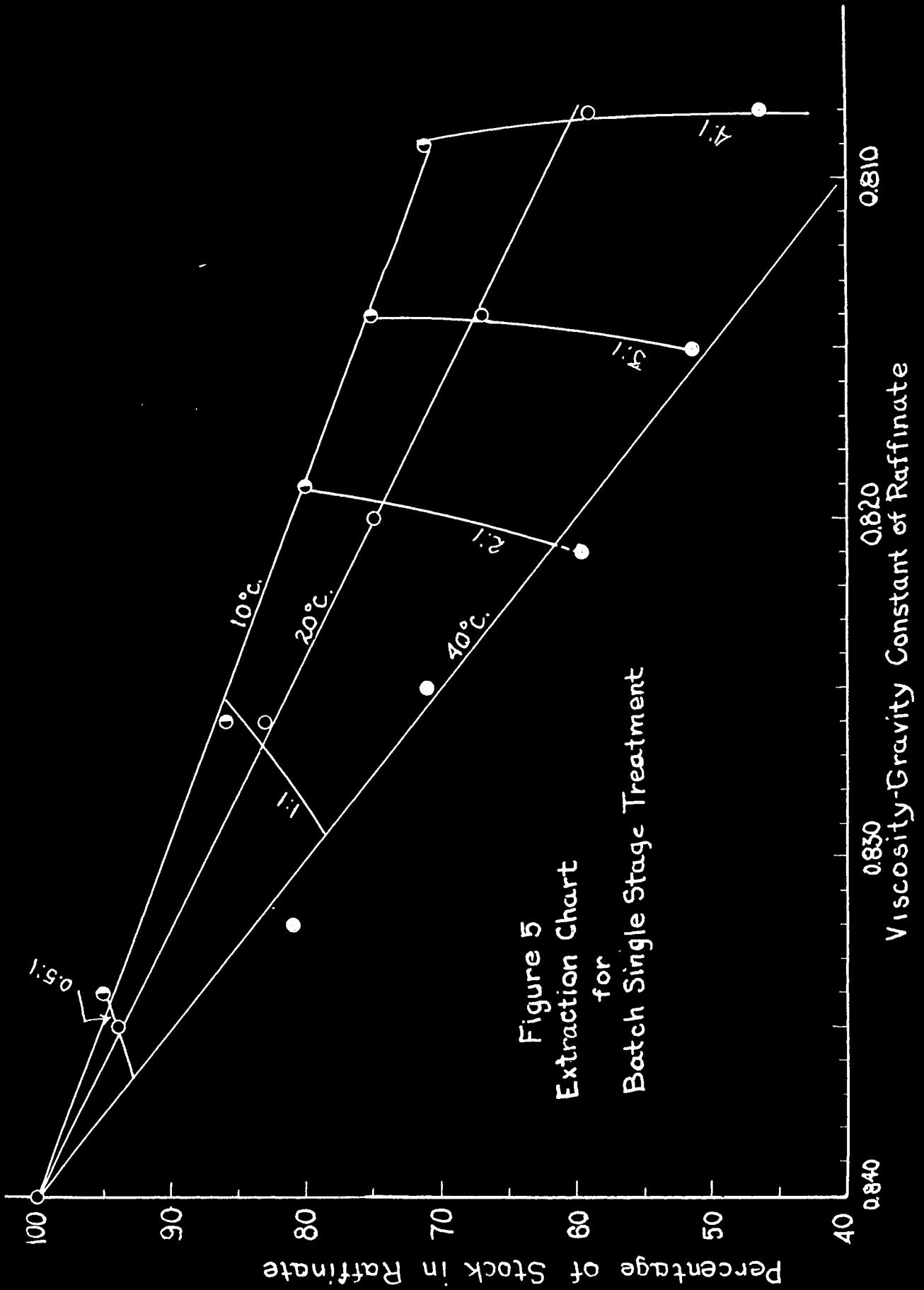| Exp. | E/R | Observed | | | | E/R | Calculated | | | |
| | | Raffinate | | Extract | | | Raffinate | | Extract | |
		V.G.C.	% Solv.	V.G.C.	% Solv.		V.G.C.	% Solv.	V.G.C.	% Solv.
16	1.01	0.817	18.1	0.937	81.4	1.03	0.815	18.7	0.941	80.5
17	1.64	0.810	18.1	0.929	85.7	1.72	0.808	18.4	0.937	84.3
18	2.44	0.808	17.8	0.938	86.5	2.36	0.805	18.2	0.933	87.0

Figure 4
Single Stage Extraction
at 10° C.
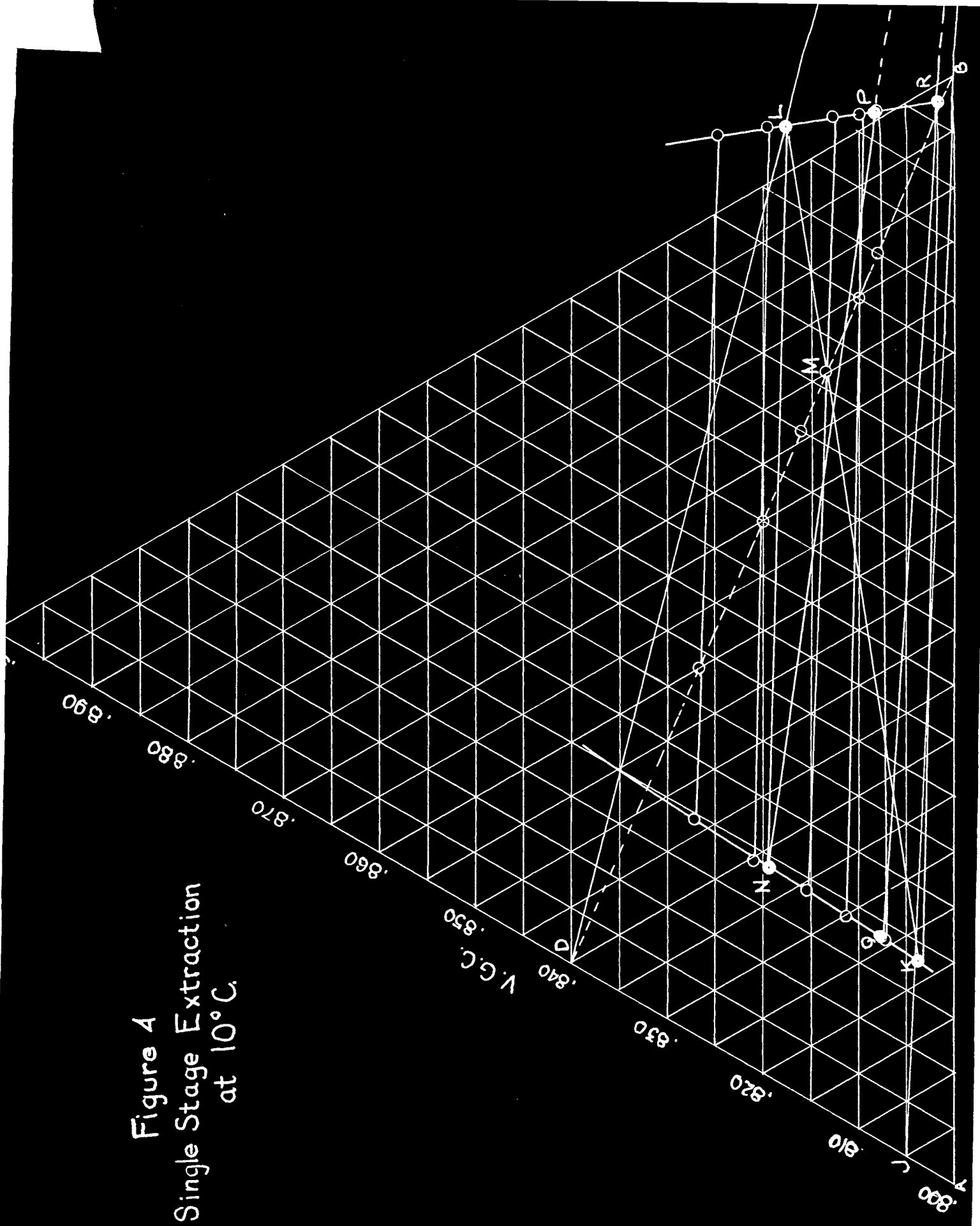
Figure 5
Extraction Chart
for
Batch Single Stage Treatment

DISCUSSION

In Figure 5, curves have been plotted showing the effect of temperature and solvent ratio upon the quality and amount of raffinate produced. This curve shows that at a given temperature if the viscosity-gravity constant is plotted against the percentage of stock in the raffinate a straight line is produced. This is in agreement with what is predicted by the fact that the viscosity-gravity constant is additive. The point for Experiment 5 lies off the straight line for 40°C. Morpholine and the stock used in these experiments are miscible at 45-50°C. Since data for the point under discussion were obtained at 40°C. and using a high solvent ratio, a high degree of accuracy should not be expected.

Data for all three extraction temperatures indicate that at 10°C. the best results were obtained for the stock used in these experiments. Poole (15) states that a high retention of solvent in the raffinate layer means impaired selectivity and that the solvent should constitute not more than 20% of this phase. The amount of solvent in the raffinate phase was lowest for the extractions at 10°C., (Figures 1, 2 and 3), and at that temperature the highest yield of raffinate for a given solvent ratio was produced without a corresponding decrease in the viscosity-gravity constant (Figure 5).

Data in Table VI show the improvement in color and the reduction in amount of carbon residue due to solvent

extraction of the stock. The colors of the raffinates obtained in the batch countercurrent extractions are especially good and the carbon residues are very low. The colors of raffinates from Experiments 15 and 18 do not align well with color determinations for the other samples.

Morpholine compares favorably with extractive solvents now in use, although at present its cost is quite high.

CONCLUSIONS

From the data presented in this thesis it can be concluded that:

(a) Morpholine does have a high selectivity as was predicted by its structure.

(b) Best results were obtained at an extraction temperature of $10^{\circ}C$.

(c) At $10^{\circ}C$., a solvent ratio of 4:1 should be used for single stage treatment to produce a highly paraffinic raffinate from the stock. For three stage batch countercurrent extraction, a ratio of between 1.5:1 and 2:1 should be used to obtain a highly paraffinic raffinate.

(d) Extraction with morpholine caused a great improvement in the color and a marked decrease in the carbon residue of the stock.

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