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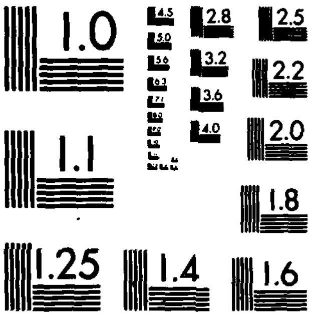

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Liquid and Solid Phase Compositions in a Partially Frozen JP-5 Fuel Low in n-Alkanes

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A JP-5 low in n-alkanes was partially frozen at several temperatures 9 to 15°C below its normal freezing point of -53°C. In spite of their low concentrations in the starting fuel, the n-alkanes were the predominant components in the solid phase crystallizing from the fuel. In this respect, this JP-5 behaves in a fashion similar to other jet fuels which contain 3 to 5 times the amounts of n-alkanes.

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Liquid and Solid Phase Compositions in a Partially Frozen JP-5 Fuel Low in n-Alkanes

CONTENTS

A1

LIQUID AND SOLID PHASE COMPOSITIONS IN A PARTIALLY FROZEN JP-5 FUEL LOW IN n-ALKANES

I. INTRODUCTION

As part of the U.S. Navy Mobility Fuels program at the Naval Research Laboratory, studies of the effect of n-alkane composition on the freezing point of fuels were carried out on several jet and diesel fuels. Results from four of these, two Shale II-derived fuels, one jet and one diesel, and two petroleum-derived fuels, also one jet and one diesel, have been reported previously (1,2). In all cases, the effect of the n-alkane concentrations was found to be similar.

In continuing these studies a fifth fuel was tested, a petroleum-derived JP-5 with very low n-alkane concentrations. The results of the tests carried out on this fuel form the subject of this report.

II. FUEL SAMPLE

The fuel used in this investigation was designated as "High Aromatic JP-5, NAPC-9." This fuel sample was received at NRL on December 21, 1981 and given the NRL No. 81-19. In this report, it will be referred to as 81-19 JP-5 fuel. The designation "high aromatic" was given the fuel merely to distinguish it from a "low aromatic JP-5" fuel, NAPC-5, which contained 15.0% aromatics. The 81-19 JP-5 fuel contained 22.67% aromatics, which is approximately the same as the 23.6% aromatics in the NRL Shale II J-22 jet fuel (3). A better designation for the 81-19 fuel would be "low n-alkane," as it contains about 4.85% n-alkanes as compared to 26.1% in NRL J-22, a Shale-II derived JP-5 fuel, and 17.5% in NRL No. 80-5, a petroleum-derived JP-5 fuel. The latter two were the jet fuels previously studied in this program. The 81-19 fuel met the military requirements for JP-5 jet turbine fuel.

The freezing point of the fuel, -53°C, was well below the specification maximum requirement of -46°C.

III. FUEL ANALYSIS

The concentrations of the n-alkanes in the original fuel samples, the filtrates and the precipitates were determined

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using a 50-meter 0.2 mm diameter fused silica capillary column in a Hewlett-Packard Model 5880 Gas Chromatograph. The inlet split-ratio was 60:1; the temperature of the column was programmed from 60°C to 186°C at 2°/min after an 8-minute initial hold; and the injector inlet and detector outlet temperatures were maintained at 325°C. Iso-octane was used as the internal standard.

Because of the complexity of this fuel (no components in the fuel comprised more than 2% by weight), it was extremely difficult to obtain reproducible chromatograms combining a flat baseline with large enough peaks to give accurate area measurements. Various size samples of the pure fuel and of samples diluted with various amounts of n-pentane were tried. In the end, it appeared that 0.1 μ-liter of undiluted fuel gave the best results. This size and type of sample was used in analyzing all the fuel, filtrate and precipitate samples.

IV. EXPERIMENTAL

When fuels of very complex composition, such as those derived from petroleum or oil shale, freeze and are no longer able to flow, a very small amount of the fuel is actually frozen into a crystalline structure; the rest, still liquid, seems to be trapped in the crystalline structure of the truly frozen material. As the temperature is lowered further below the freezing point, the fraction actually frozen increases. Because the solid material cannot be completely filtered or otherwise separated from the entrapped liquid, the major problem is to determine the amount of crystalline solid material actually present. This can only be done by an indirect method, based on the assumption that there are compounds (markers) in the fuel that have sufficiently low freezing points that they remain completely in the liquid state at the various low temperatures used. To determine such fuel components, designated by the letter 'k' (1), was a major primary task of this work.

The Liquid-Solid Separator (or LSS), developed by Van Winkle and Affens (1), was used to separate the purely liquid fraction, referred to as "filtrate," from the "precipitate," the fraction containing all the solidified, or crystalline, material plus the liquid entrapped in the crystalline structure. The method used to effect this separation was essentially the same for all fuels.

V. RESULTS AND DISCUSSION

A GC chromatogram for the 81-19 fuel is shown in Figure 1. The chromatograms for the filtrates and precipitates are very similar, showing major peaks for the n-alkanes from C_{11}

to C_{15}, with lesser peaks for C_9, C_{10} and C_{16}. The peak for C_{17} is very small, and does not appear in the filtrate chromatograms.

Several major peaks other than the n-alkane peaks also appear on the chromatogram. Seven of interest are labeled 'a' through 'h'. These peaks were studied with the view to using the corresponding fuel components as candidates for the 'k'-component, as discussed below.

A. n-Alkane Concentration in Filtrate

The concentrations of all components in the original fuel and in the filtrates could be determined directly from the chromatograms, based on the internal standard. The concentrations of the n-alkanes in the original fuel are listed in Table I. Also included in this Table are the normalized concentrations for the filtrates at six different sub-freezing temperatures. The normalized values are defined as the ratio of a specific n-alkane (C_{10} to C_{16}) in the filtrate, precipitate, or solid to its concentration in the starting fuel.

In Figure 2, the logarithm of the filtrate concentration of each n-alkane (C_{12}-C_{16}) is plotted against the reciprocal of the absolute temperature (°K). The concentrations in the filtrate at the freezing point of the fuel (-53°C) should be the same as the concentrations in the original fuel, since at the freezing point only an infinitesimal amount of solid is present. Therefore, the concentrations of the 5 n-alkanes in the fuel are included in Figure 2 as the concentrations at the freezing point. They were not, however, included as points on the lines when linear regression was used to determine the slope and position of the lines through the points.

It can be seen that the data for four of the n-alkanes (all except C_{13}) form straight lines, as would be expected in a Van't Hoff solubility plot. The line for the smallest n-alkane (C_{12}) is almost horizontal, as would be those for C_{10} and C_{11}, were they included in the Figure. The horizontal line suggests little or no change in C_{12} concentration with temperature in the freezing-point region which was investigated (-62°C to -68°C).

The higher alkanes, C_{14}-C_{16}, however, show definite slopes which increase in magnitude with the carbon number. These results are in close agreement with the results from the fuels previously studied (1,2).

The data for tridecane, C_{13}, follow a different pattern, as is evident in Figure 2. Not only are the data widely scattered from the straight line obtained by linear regression from the six data points, but the line itself shows a slight increase in concentration with decreasing temperature. Also, the extrapolated concentration at the freezing point is considerably lower than the n-C_{13} concentration in the fuel. The other four n-alkanes indicate, by extrapolation, concentrations either very close to the fuel concentrations (C_{12} and C_{16}) or somewhat greater (C_{14} and C_{15}). This suggests that n-C_{13} may have an opposite effect on the freezing point of fuels to that of the other n-alkanes. This anomalous effect of n-C_{13} has been reported elsewhere (4,5), where the effect of n-C_{13}, in certain cases, was to lower the freezing point rather than to raise it.

An alternate explanation for the anomalous data on C_{13} relates to problems with GC analysis. The determination of the concentration of n-C_{13} in the fuel, in the filtrate, and in the precipitate presented serious difficulties. Not only was there considerable drift in the baseline, but there was also a noticeable unresolved "shoulder" on the C_{13} peak on the chromatograms. While the peaks for the n-alkanes C_{11}, C_{12} and C_{14} were also located in a region of baseline drift, there were clear valleys on both sides of the peaks and no shoulders. Hence, the quantitative accuracy of analysis of the n-C_{13} peaks was considerably less than that of the other n-alkanes. Furthermore, the trace in the GC-mass spectrogram showed a peak so closely associated with the n-C_{13} peak that it was not distinguishable on the GC trace used for quantitative analysis. This other peak appears by mass spectrometry to be a substituted indane. This hydrocarbon would not be expected to form any crystalline solid at the temperatures investigated, but should instead be concentrated in the filtrate, not in the precipitate. For n-C_{13} just the opposite is to be expected. As a result, the calculated concentrations of n-C_{13} are probably not accurate. The line for n-C_{13} in Figure 2 is therefore shown as a dotted line, and is probably not indicative of the true behavior of n-C_{13}. Moreover, the upward slope of the line could also be due to the presence of the indane.

The concentration of n-C_{13} was considerably greater in the four other fuels previously investigated and therefore any effect of an unresolved component, if it were present in those fuels, would probably be masked and go unnoticed.

The normalized data for each n-alkane in Table I bear out the conclusions reached from Figure 2. The normalized concentration for each n-alkane, except n-C_{13}, going from left to right approach unity when extrapolated to the freezing point of -53°C. The descending columns in Table I show decreasing normalized concentrations as the carbon number increases. n-C_{13} shows the peculiar behavior described above. Therefore, the filtrate data in general, both in Figure 2 and in Table I, reinforce earlier conclusions regarding the importance of the role of the higher n-alkanes in jet fuel freezing.

B. Precipitate Considerations

Van Winkle and Affens (1) developed an experimental/ mathematical procedure to estimate the fraction of liquid trapped in the precipitate collected in the LSS. That procedure has been followed in this report also. Briefly, that procedure utilizes 'Z', the weight fraction of liquid trapped in the precipitate as definied by equation (a):

$$W_L = ZW_P \qquad \text{(a)}$$

where W_L is the weight of liquid in the precipitate and W_P the weight of precipitate. The composition of W_L is the same as that of the filtrate, W_F.

'Z' is determined from experimental measurements on hydrocarbon species in the fuel which do not crystallize at the freezing temperatures used. These fuel markers, designated as 'k'-components, give the value of 'Z' from equation (b):

$$Z = X_P(k)/X_F(k) \qquad \text{(b)}$$

where $X_P(k)$ and $X_F(k)$ are the concentrations of the marker in in the precipitate and filtrate, respectively.

Use of measured concentrations of a specific n-alkane in the filtrate, $X_F(A)$, and precipitate, $X_P(A)$, along with 'Z' gives the concentration of the n-alkane in the solid fraction, $X_S(A)$, of the precipitate by the following equation:

$$X_S(A) = (X_P(A)-ZX_F(A)/(1-Z) \qquad \text{(c)}$$

C. Selection of 'k'-Component

In order to identify the seven large peaks labeled 'a' to 'h' on the chromatogram in Figure 1, mass spectroscopy was used. The components responsible for these peaks were identified as follows:

'a': C_4 substituted benzene
'b': a substituted cyclohexane
'c': methyl decalin plus a C_4 substituted benzene
'e': mixture of several components
'f': " " " "

'g': mixture of several components
'h': methyl tetralin or dimethyl indane plus a C_6 substituted benzene

Although there is some uncertainty in the identification of these compounds, the basic structures determined by mass spectroscopy indicate compounds with freezing points well below the temperatures at which the experiments were carried out. Thus, it seemed as though each of these components should be a satisfactory marker for the definition of 'Z'.

In practice, however, it was not easy to determine the value of 'Z'. The concentrations of all seven compounds ranged from 0.7% to 2.0%, very low compared to the 'k'-components used for the other four fuels. After a careful study of the chromatograms, the components 'a', 'c' and 'e' were selected as 'k'-components. These had residence times longer than n-C_{10} and shorter than n-C_{12}. The 'k' species for fuel 81-19 are different from those used in earlier work (1). The peaks for 'a', 'b', 'c' and 'e' were located on the chromatogram where the baseline was beginning to drift; the other three 'k'-component candidates were where the baseline drift was most pronounced. The value of 'Z' for each experimental run was determined by taking the average value of 'Z' calculated from peaks 'a', 'c', and 'e'. At the lowest temperature, -67.6°C, only 'a' and 'c' gave values of 'Z' less than unity, and so the average value of these two was used.

D. Solids: Amount and n-Alkane Concentrations

With the value of 'Z', the fraction of liquid in the precipitate, thus obtained, the percent of the fuel that had actually frozen, or crystallized, was calculated for each temperature. Table II lists these calculated values, which are plotted against temperature in Figure 3. The straight line in the Figure was calculated by linear regression analysis.

Using the values of 'Z', the concentrations of the n-alkanes in the solids were calculated by equation (c). These data are listed in Table III.

The fraction of each n-alkane originally present in the fuel that has crystallized into the solid was then determined. Figure 4 shows this fraction of the n-alkanes in the solids as a function of temperature. The straight lines are based on linear regression analysis.

The amount of solid crystalline material increases very slightly with decreasing temperature for the fuel 81-19 JP-5 compared with the other two jet fuels tested. For example, at

10°C below the freezing point only 1.3% solid crystalline material was formed in the 81-19 fuel, whereas for the petroleum-derived 80-5 JP-5 there was 6.5% solids and for the Shale II-derived J-22 there was 9.0% solids. Thus, the actual amount of crystalline solids increases with the total amount of higher n-alkanes present in JP-5 fuel, which is to be expected if only the higher n-alkanes freeze out.

The separation of the filtrate from the precipitate in the LSS was easiest for the J-22 fuel, next easiest for the 80-5 JP-5 fuel, and most difficult for the 81-19 JP-5 fuel. Thus, it became increasingly difficult to effect a good separation as the amount of higher n-alkanes in the fuel decreased. The separation of the filtrate from the precipitate fraction of the 81-19 JP-5 fuel was so far from complete in every run that the value of 'Z' was too close to unity to permit accurate quantitative calculations. This is evident from the scattering of the data points in Figures 3 and 4. The trends are clearly evident, but the accuracy achieved with the four previously tested fuels is lacking for fuel 81-19.

In the previous four fuels, the n-alkanes could account for roughly 90% of the composition of the crystalline solids formed. In many cases it was even greater, indicating that the solids were composed of n-alkanes only, within the limits of experimental error. The chromatograms were carefully examined in all cases to ascertain whether any peaks other than those of the larger n-alkanes were relatively greater in concentration in the precipitate than in the filtrate. This would indicate an increased concentration in the precipitate which could only mean that such compounds formed part of the crystalline solids. No such peaks were found. Hence, it could be concluded that only the large n-alkanes actually froze or crystallized out of the solution.

In the case of the 81-19 JP-5 fuel, the calculated total percentage of n-alkanes in the solids varied from 49% to 98%, the average value being 66%. Again, the chromatograms were studied for peaks, other than the n-alkanes, which were enhanced in the precipitate. Once more none were found, so that no components comprising so much as 0.2% by weight in the fuel could be identified as forming part of the solid material. Thus, the chromatograms indicate that only the higher n-alkanes formed the solid material.

The inaccuracies in the calculated values of the concentrations of n-alkanes in the solid material can most probably be attributed to the very high values of 'Z' obtained for this fuel. A total material balance summary is given in Table IV for the experimental runs made with the 81-19 JP-5 fuel. In all cases the recovery is 99% or better, similar to that of the other four fuels (2). In the Table are included the values of 'Z' obtained for each run. As 'Z' is a fraction of liquid in the precipitate, it can easily be seen that the separation was poor, and that the fraction of solids in the precipitate was extremely small. Equation (c) shows that as 'Z' approaches unity, the denominator becomes small. In such a case, a small error in 'Z' effects a much larger error in $X_S(A)$. Thus, a high potential error is possible at this point in all calculations. Therefore, it seems correct to conclude that for the 81-19 JP-5 fuel, as for all the others tested, only the larger n-alkanes freeze, or crystallize, and form solid material at the temperatures investigated.

VI. CONCLUSIONS

The solid matrix formed when fuels freeze is obviously of great importance as regards the flow characteristics of the fuel. If the larger n-alkanes are the only components to form crystalline solids at temperatures as much as 10 to 20°C below the freezing point, and if the actual solid material amounts to less than 10% of the total precipitate, then the crystalline lattice must be of such a structure that it can hold within it a very large amount of liquid and cause the whole mass to act as a solid.

It is clear from these studies that fuels freeze and lose their ability to flow at temperatures only slightly below the freezing point, even though only a very small amount of actual solid or crystalline material is formed. In order to lower the pour point, or temperature at which the fuel flows freely, it appears that studies should be carried out on the clathrate type of structure that seems to be formed even by the freezing of very small amounts of n-alkanes. Such a structure is capable of trapping much of the liquid and thereby immobilizing it. If that structure could be changed or broken in some way, it might be possible for jet fuels to be used at temperatures well below their freezing points.

The freezing point of jet fuel is significantly influenced by the amounts of large n-alkanes in the fuel. Further, from these studies, it must be concluded that the large n-alkanes present in the fuel exert major control on the pour characteristics of the fuel below its freezing point.

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Table I. n-Alkane Concentrations in Filtrate of 81-19 JP-5 as Function of Temperature

		Normalized Concentrations (% W/W)*						
n-Alkane	Original Fuel Sample (% W/W)	-67.6°	-65.9°	-65.7°	-64.4°	-63.3°	-62.1°	-53.0°**
C_{10}	0.21	0.99	1.07	1.03	1.05	1.04	1.01	-
C_{11}	0.82	1.03	1.05	1.02	1.07	1.09	1.02	-
C_{12}	1.01	0.92	1.03	0.99	0.98	0.98	1.00	1.08
C_{13}	1.30	0.63	0.70	0.81	0.81	0.64	0.61	0.62
C_{14}	0.82	0.52	0.57	0.63	0.67	0.75	0.72	1.35
C_{15}	0.45	0.25	0.32	0.34	0.38	0.42	0.50	1.42
C_{16}	0.16	0.18	0.22	0.24	0.25	0.30	0.37	1.11
C_{17}	0.06	-	-	-	-	-	-	-

*Normalized data - concentration divided by concentration in original fuel sample

**Data extrapolated to freezing point (-53°C)

Table II. Percent Solids as Function of Temperature

Fuel: 81-19 JP-5

T, °C	% Solids (W/W)
-53.0	0*
-62.1	0.84
-63.3	1.43
-64.4	1.67
-65.7	2.11
-65.9	1.91
-67.6	1.87

* Freezing point of fuel

Table III. Percent of Total Fuel n-Alkanes Found in Solid Phase

Fuel: 81-19 JP-5

n-Alkane	-62.1°C	-63.3°C	-64.4°C	-65.7°C	-65.9°C	-67.6°C
C_{13}	14.0	12.0	11.4	12.9	16.2	24.6
C_{14}	28.6	30.9	34.8	41.9	41.7	49.2
C_{15}	51.5	59.6	63.9	66.4	71.3	76.9
C_{16}	65.1	72.6	74.8	75.0	80.3	83.2
C_{17}	77.6	83.4	87.3	86.0	93.0	92.4

Table IV. Total Material Balances

Fuel: 81-19 JP-5

T, °C	-67.6	-65.9	-65.7	-64.4	-63.3	-62.1
% Filtrate	66.7	65.1	72.7	69.4	79.7	86.3
% Precipitate	32.2	33.6	26.5	29.6	19.8	13.3
% Recovery	98.9	98.7	99.2	99.0	99.5	99.6
% Solid	1.89	1.91	2.11	1.67	1.43	.84
'Z'	.942	.944	.921	.944	.928	.937

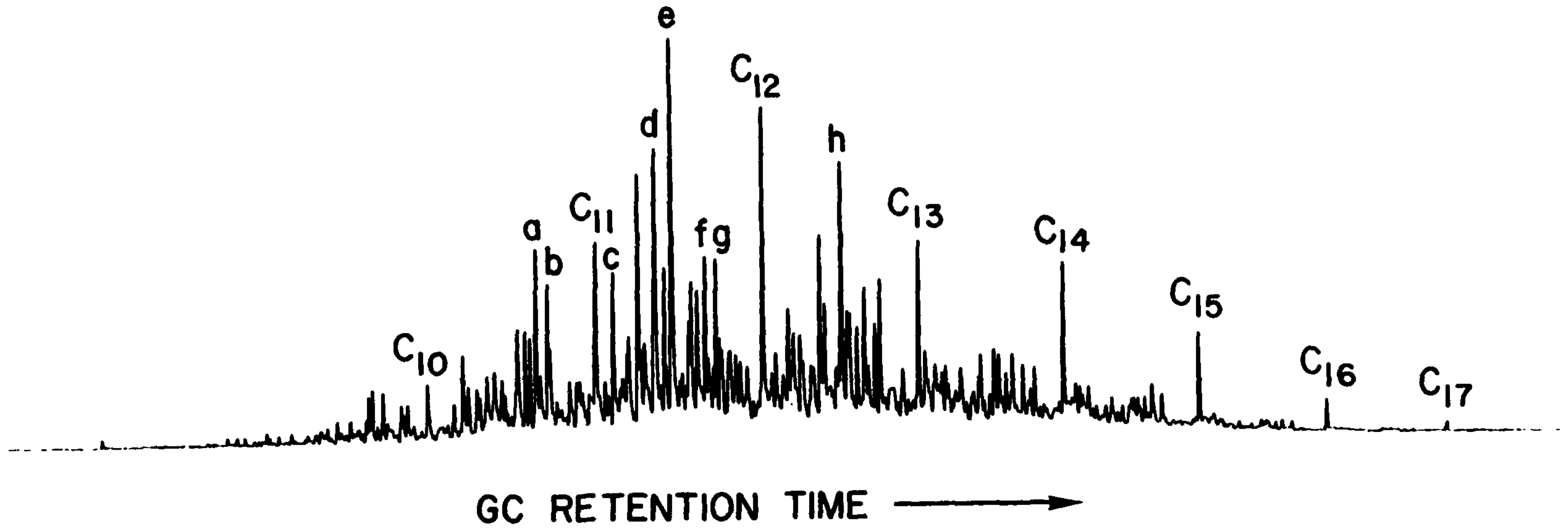


Fig. 1 — Gas chromatogram of low n-alkane JP-5 (81-19)

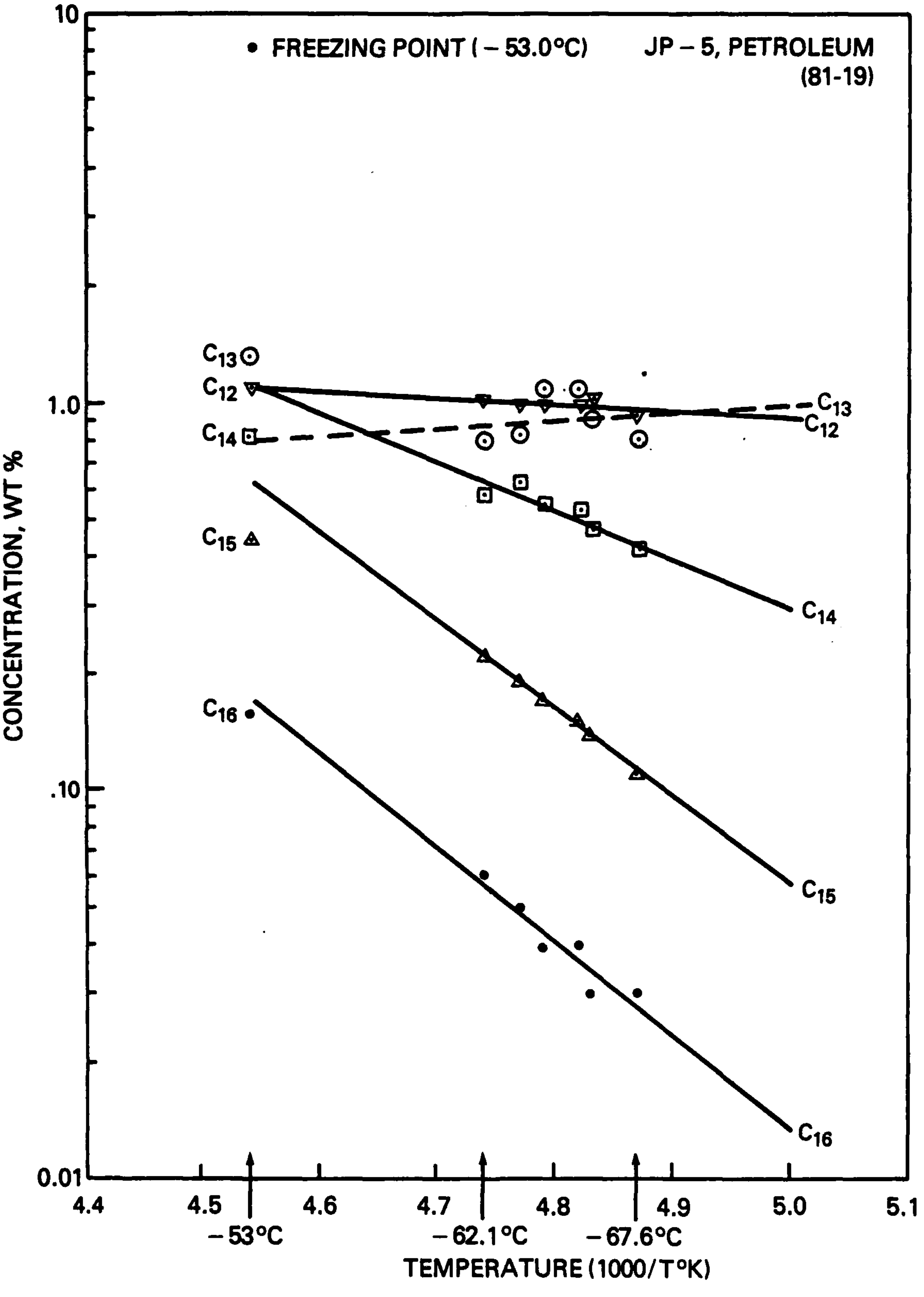


Fig. 2 — n-Alkanes in filtrate

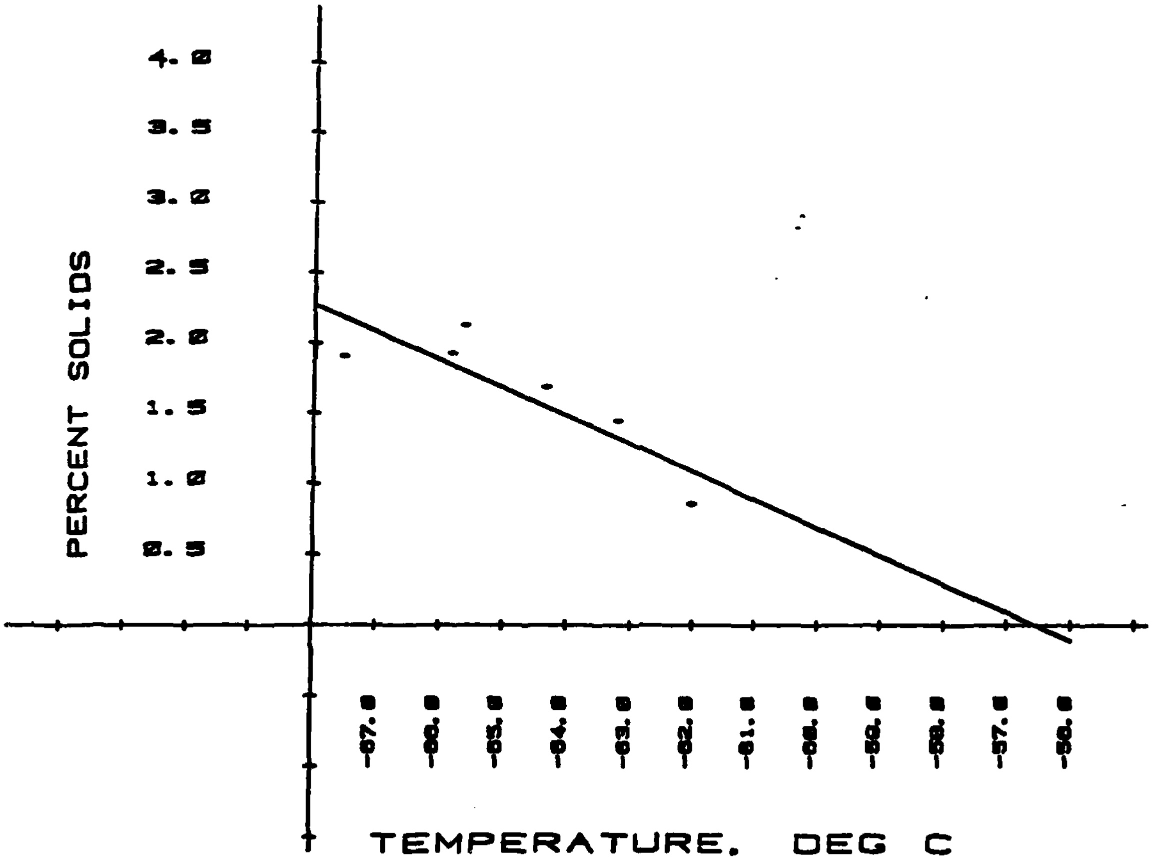


Fig. 3 — Percent solids vs temperature. Petroleum derived JP-5 (81-19).

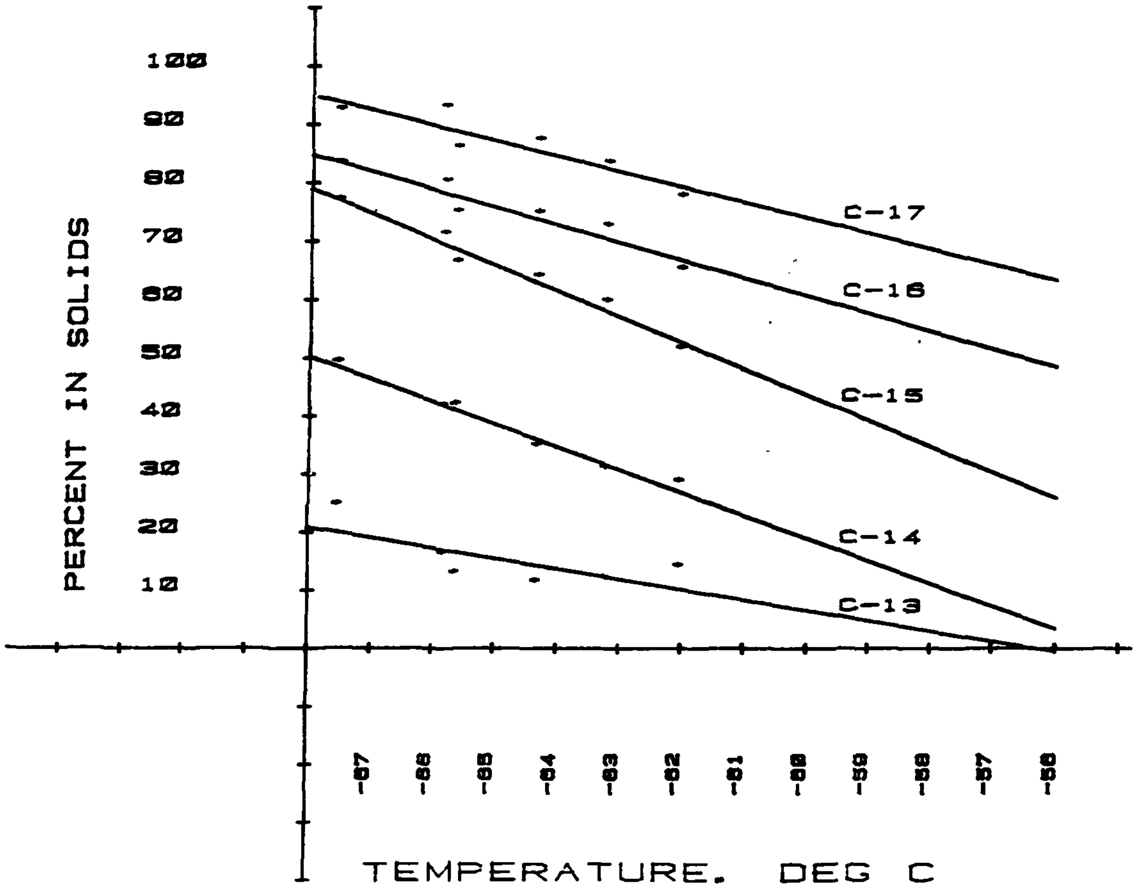
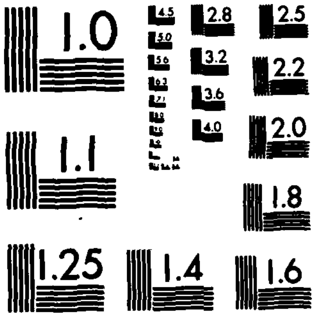


Fig. 4 — Percent of total fuel n-alkanes found in solid phase fuel 81-19.



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