

Effect of Composition on Freezing Points of Model Hydrocarbon Fuels

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INTRODUCTION

Freezing Points of Jet Fuels

Jet aircraft are frequently exposed to low operating temperatures and it is essential that their fuels not freeze in these environments. Plugging of filters, pumpability, and related fuel system operational problems are dependent on freezing point, and for this reason, jet fuel specifications include requirements for maximum freezing point. Commercial jet fuel (Jet A, Aviation Turbine Fuel, ASTM D 1655-80), for example, is required not to freeze above -40°C . Military jet fuels, because of world wide operations, have even lower temperature requirements. The maximum acceptable freezing points for Air Force fuels (JP-4 and JP-8 Aviation Turbine Fuels, MIL-T-5624L and MIL-T-83133A respectively) are -58° and -50°C ; and the Navy's JP-5, (MIL-T-5624L, High Flash Point Aviation Turbine Fuel) has a maximum of -46°C .

The low temperature properties of a jet fuel (freezing point, pour point, viscosity), as well as some of its other properties, are controlled by the nature and concentrations of its components (chemical composition). Unfortunately, many components of a fuel which tend to lower freezing point (smaller hydrocarbons of higher vapor pressure), will also lower the flash point. In the case of JP-5, because of its relatively high minimum requirement for flash point (60°C) for reasons of ship safety, and its low maximum requirement for freezing point (-46°C), it is not always practical to produce JP-5 from all available crudes. These restraints limit the amount of JP-5 which can be produced from a barrel of crude oil and the problem exists for both conventional JP-5 (from petroleum) and for JP-5 from syncrudes.

Freezing Point and Composition

It has been known that molecular size and symmetry play an important part in the phenomenon of crystallization from solution and that this also applies to solutions of hydrocarbons. Dimitroff et al (1,2), studying the effect of composition on several types of fuels, found that the saturate fraction exerted the greatest influence on raising the freezing point and that the presence and amount of high-temperature freezing hydrocarbons had a major influence. They reported that in some cases the aromatic fraction was important and that in general all hydrocarbons play a part in fuel crystallization. Petrovic and Vitorovic (3) found a correlation between the sum of the concentrations of the three largest straight chain alkanes and freezing point in the jet fuels which they studied. Antoine reported on studies of 32 samples of jet

fuel derived from oil shale and coal syncrudes (4) and concluded that the concentrations of the long straight chain molecules in the fuels exert influence on the freezing point but are not the complete controlling factor. Solash et al (5) at this laboratory investigated jet fuels derived from various sources and reported that the freezing points were related to the amount of the largest n-alkane present (but not the total n-alkane concentration) in these fuels. These findings were not in agreement with the correlation of Petrovic and Vitorovic. Solash et al plotted $\log(\text{mol}\% C_{16})$ vs. the reciprocal freezing point of 11 fuels and found reasonable adherence to a solubility plot. They concluded that the freezing point of a fuel is not a simple function of fuel composition and that much more work must be done before a coherent theory of freezing point can be developed for multi-component mixtures.

It was decided to extend our freezing point studies to model hydrocarbon fuel mixtures, with emphasis on the higher n-alkanes, in order to learn more concerning the effect of composition on freezing point.

EXPERIMENTAL

Defining Freezing Point

"Freezing Point," as applied to jet fuels and related mixtures, is defined by the ASTM (6) as "...that temperature at which crystals of hydrocarbons formed on cooling disappear when the temperature of the fuel is allowed to rise". This, of course, is really a "melting point," since "freezing point" is the temperature at which crystals start to crystallize out. However, the two phenomena take place at almost equivalent temperatures, and the term "freezing point" will be used here because of its wide use in the fuel literature.

Determination of Freezing Point

Freezing points were determined by the ASTM method D2386 for aviation fuels (7) with some modifications. Temperature readings were made by means of a thermocouple (Type "J") - potentiometer-recorder system, and liquid nitrogen was used as the refrigerant. Stirring was done mechanically.

Hydrocarbons

The hydrocarbons used were 99% pure grade. The decalin (decahydronaphthalene) was found to consist of 62.7% (w/w) of the trans isomer and 37.3% cis isomer by gas chromatography. The "Isopar-M" kerosene consisted of a relatively high boiling, low freezing, narrow-cut isoparaffinic solvent whose average molecular weight was 191 (8).

RESULTS AND DISCUSSION

n-Alkanes in Isopar-M

Solutions of six n-alkanes ($C_{12} - C_{17}$) in Isopar-M at various concentrations (mol %) were prepared and their freezing points (T_m) determined. Reciprocal freezing points ($1/T_m$) vs log of concentrations are plotted in Figure 1 for each alkane. The temperature scale (ordinate) of the graph is reversed in order to show temperature increase going up the graph. It is seen in the figure that the data points fit the straight lines fairly well so that there is good adherence to a typical solubility plot (ideal freezing point curve). The lines shown in the graph were derived by means of a linear regression treatment of the data and are a best fit of the data. From their slopes and intercepts, heats (ΔH_m) and entropies (ΔS_m) of fusion and extrapolated freezing points ($T_{m,0}$) of the pure alkanes were calculated by means of the Van't Hoff ideal solubility equation (9-12), and the thermodynamic relationship between ΔS_m , ΔH_m and $T_{m,0}$ (13).

$$\ln X = - \frac{\Delta H_m}{RT_m} + \frac{\Delta H_m}{RT_{m,0}} \quad 1)$$

$$\Delta S_m = \frac{\Delta H_m}{T_{m,0}} \quad 2)$$

where R is the gas constant, and X represents molar concentration. This approximate equation, which describes the variation of freezing point with concentration, is based on several simplifying assumptions including that ΔH_m is independent of temperature, and that Raoult's law is obeyed. Derived freezing point data from the Isopar-M solutions are shown in Table I with literature values of pure n-alkanes (13, 14) shown for comparison.

It is seen in the table that the experimentally derived and literature $T_{m,0}$ values are in good agreement, but this is not always the case for ΔH_m and ΔS_m . For ΔH_m and ΔS_m , the agreement is good only for the even carbon numbered alkanes, but there is poor agreement for the odd numbered compounds. It has long been known (9) that freezing and melting point data of pure compounds in some homologous series often exhibit the phenomenon of "alternation". In these series, such as the n-alkanes, with each additional CH_2 group, alternately small and large increases in a given property are observed (9). This can be seen for each of the three properties in Table I for both the literature data for the pure alkanes, and the values derived from the Isopar-M solution freezing points. It has been shown (9) for the higher members of a homologous series, that ΔH_m and ΔS_m values fall on two linear curves when plotted against carbon number. In this work, the odd and the even carbon numbered alkane data also form two separate straight lines respectively when ΔH_m or ΔS_m are plotted against carbon number. There was, however, a much wider variation between the odd and even data points for the literature values than between that of the experimentally derived points in this study.

Solvent Effect

In a second set of freezing point experiments, the effect of solvent was investigated. Solutions were prepared for *n*-tetradecane, *n*-hexadecane, and naphthalene in different solvents and at several concentrations. In the case of *n*-hexadecane, some mixed solvents were also used and their compositions are shown in Table II. Freezing point data were plotted in the same manner as that of the alkanes in Isopar-M. Some of the *n*-hexadecane data for single solvents are shown in Figure 2. It is seen in the figure that the straight lines plotted fit the data fairly well for these four plots and this was also true for the other solutions. The solvent effect experimental data (T_m and X) were also treated by linear regression and the derived T_m^o freezing point data are shown in Table III. For each of the three solutes, the solvents are listed in order of increasing ΔH_m . Literature data (13, 14) for the pure solutes are included in the table for comparison. An examination of Figure 2 and Table III shows considerable variation in the derived data for each of the solutes in the different solvents. When a solid dissolves in a liquid and an ideal solution is formed, the process may be considered equivalent to melting of the pure solute at the lowered temperature at which solution is taking place, and the ideal solubility equation implies this concept (9-12). From the ideal solubility equation (or from the solubility plots in Figures 1 and 2), it follows that relative solubility bears an inverse relationship with T_m . At a given concentration, for a relatively good solvent, solution (melting) will take place at a lower temperature than that of a relatively poorer solvent. Similarly, at a given temperature, it can be shown that solubility increases with decreasing ΔH_m for systems which obey the ideal solubility equation. In general, both T_m^o and ΔH_m are approximate measures of relative solubility. For example, in Figure 2, it is seen that decalin (the lowest curve in the figure) is a relatively better solvent for *n*-hexadecane than secondary butyl benzene (the upper curve). The data in Table III also illustrate this concept. For C_{14} , in the three solvents shown in the table, *n*-heptane and Isopar-M are good solvents, and secondary butyl benzene, an aromatic compound, the poorest. The T_m^o for C_{14} in Isopar-M (280°K) is the same as that of the literature value for the pure C_{14} (279°K) within experimental error. For C_{16} in individual solvents, *n*-heptane, decalin and Isopar-M appear to be relatively good solvents, and secondary butyl benzene the poorest. The T_m^o values derived for decalin (289°K) and Isopar-M (290°K) solutions are the same as that of pure C_{16} within experimental error, but the *n*-heptane result (295°K) seems to be high. For C_{16} in mixed solvents, Solutions A, B and C are relatively good solvents, and Solution G the poorest. As seen in Table II, Solutions A, B and C consist chiefly of Isopar-M or Isopar-M and decalin which were shown above to be relatively good solvents for C_{16} . Again, the aromatic (Solution G) was the poorest. For naphthalene, as might be expected, Table III shows that secondary butyl benzene is a better solvent than Isopar-M. The T_m^o derived from the secondary butyl benzene solutions (374°K), however, is much higher than that of pure naphthalene (354°K). The naphthalene data are limited, however, to only two solvents at a limited number of concentrations.

Tertiary Solutions

In order to observe possible interaction between n-alkanes in a common solvent and its effect on freezing point, solutions of n-C₁₃ and n-C₁₆ in Isopar-M were prepared at several concentrations. Standard freezing point plots of 1/T_m vs. Log n-C₁₃ at several constant C₁₆ concentrations are shown in Figure 3. The 0% C₁₆ line in the graph is the curve for C₁₃ in Isopar-M from Figure 1. It is seen in the figure that the 0.17% C₁₆ data points fall on a parallel straight line, but at somewhat lower temperatures than that of the pure C₁₃ line. However, a change is observed for higher C₁₆ concentrations. The 0.42% C₁₆ curve consists of two lines of opposite slopes. The section of the curve above about 3% C₁₃ falls on the 0.17% C₁₆ line. The 0.84% and 1.69% C₁₆ data follow the pattern of the 0.42% C₁₆ curve but with decreasing slopes. The 4.25% C₁₆ line is horizontal, showing that changes in C₁₃ concentration have no effect, and that the C₁₆ has "taken over" the control of freezing point.

Two interesting observations were noted in Figure 3. First, for C₁₆ concentrations of 0.42, 0.84, and 1.69% C₁₆, addition of C₁₃ at the lower C₁₃ concentrations causes a reduction of freezing point. The second observation, which was unexpected, is that certain combinations of C₁₃ and C₁₆ in Isopar-M freeze at lower temperatures than that of the same concentration of either alkane alone in the same Isopar-M base stock. For example, the freezing point of 1.04% C₁₃ and 0.17% C₁₆ in Isopar-M was 207°K, whereas the freezing point of 1.04% C₁₃ (C₁₆ = 0) was 209°K and that of 0.17% C₁₆ (C₁₃ = 0) was 225°K. A similar solution of 3.11% C₁₃ + 0.42% C₁₆ froze at 218°K, whereas the freezing points of the single alkanes in Isopar-M were 221°K and 233°K respectively for 3.11% C₁₃ and 0.42% C₁₆.

The data in Figure 3 suggest that there has been interaction between the C₁₃ and C₁₆ in their mutual influence on the freezing points in Isopar-M solutions.

The freezing point-concentration plots for C₁₃ and C₁₆ in Isopar-M (Figure 1) show relatively close adherence to the ideal solubility equation suggesting a minimum of interaction between the individual solutes and solvent for either alkane. But, when together in the same solution, their mutual behavior is unexpected. The mutual solubility of two compounds is a qualitative measure of the extent of the interaction between their molecules, varying from simple departure from ideal behavior to actual compound formation between the two substances (12). In some cases, it is possible to explain deviations from ideality. Most commonly, the explanation is based on association to form dimers or trimers; compound formation between solute and solvent; or possibly dissociation of the solute to form two or more molecules (11). The last of these possible explanations (dissociation), however, would not be expected to apply to solutions of alkanes in hydrocarbon solvents. Another possible explanation is that the two alkanes form a eutectic type mixture. In the case of the C₁₃-C₁₆ in Isopar-M behavior, this is now under investigation. It is hoped that by isolating the crystals which form during freezing, and identifying them, an explanation of this behavior might be forthcoming. This work is still in progress.

SUMMARY AND CONCLUSIONS

A study was made of the effect of composition on the freezing points of model hydrocarbon jet fuel type mixtures. Solutions of higher n-alkanes (C_{12} - C_{17}) in several solvents were emphasized. Freezing points (T_m) of solutions of single alkanes were found to conform with the Van't Hoff ideal solubility equation. From the slopes and intercepts of plots of concentration ($\ln X$) vs $1/T_m$, heats (ΔH_m) and entropies (ΔS_m) of fusion, and extrapolated freezing points of pure alkanes ($T_{m,0}$) were derived. For an isoparaffinic base solvent (Isopar-M), the derived $T_{m,0}$ values were in good agreement with the literature values for the pure alkanes. For ΔH_m and ΔS_m , only the even carbon numbered alkanes exhibited values similar to literature data for the pure compounds. This alternating behavior for the n-alkanes series has been observed for melting point and other properties of the pure compounds. For alkanes in other solvents, considerable solubility effect was noticed. For C_{14} and C_{16} , decalin and Isopar-M were found to be relatively good solvents but aromatic compounds, such as butyl benzenes, were relatively poor. For naphthalene, butyl benzene was a better solvent than Isopar-M. For mixtures of C_{13} and C_{16} in Isopar-M, significant changes or reversals of slope were observed for $1/T$ plotted against $\ln X$ (C_{13} concentration) at various C_{16} concentrations, and this suggested interaction between the two alkane solutes. C_{16} had the predominant effect in $C_{13} + C_{16}$ solutions in Isopar-M. Above about 4% C_{16} , changes in C_{13} concentration had no observable effect.

REFERENCES

1. Dimitroff, E., Gray, Jr., J. T., Meckel, N. T., and Quillian, Jr., R. D., 7th World Petroleum Congress, Mexico City, April 1967, Individual Paper No. 47.
2. Dimitroff, E. and Dietzman, H. E., American Chemical Society, Petroleum Division, Preprints, 14, B-132 (1969).
3. Petrovic, K. and Vitorovic, D., J. Inst. Pet. 59, 20 (1973).
4. Antoine, A. C., "Evaluation of the Application of Some Gas Chromatographic Methods for the Determination of Properties of Synthetic Fuels," NASA Technical Memorandum 79035, November 1978.
5. Solash, J., Hazlett, R. N., Hall, J. M. and Nowack, C. J., Fuel, 57, 521 (1978).
6. American Society for Testing and Materials, Compilation of ASTM Standard Definitions, 4th Ed, 1979.
7. American Society for Testing and Materials, "Freezing Point of Aviation Fuels," ASTM D 2386-67.
8. Humble Oil and Refining Co., Isopar-M, Data Sheet DG-1P, 1968.
9. Cines, M. R., "Solid-Liquid Equilibria of Hydrocarbons," Chap. 8, Physical Chemistry of the Hydrocarbons, A. Farkas, Ed., Academic Press, New York, 1950, pp. 315-362.

10. Williams, A. G., "An Introduction to Non-Electrolyte Solutions," Wiley, New York 1967.
11. Skau, E. L. and Wakeham, H., "Determination of Melting and Freezing Temperatures," Chap. III, Physical Methods of Organic Chemistry, Techniques of Organic Chemistry, A. Weissberger, Ed., Vol. I, Part I., Interscience, New York, 1949, pp. 49-105.
12. Vold, R. D. and Vold, M. J., "Determination of Solubility," Chap. VII, Physical Methods of Organic Chemistry, Techniques of Organic Chemistry, A. Weissberger, Ed., Vol. I, Part I, Interscience, New York 1949, pp. 297-308.
13. Rossini, F., Pitzer, K. S., Arnett, R. L., Braun, R. M. and Pimentel, G. C., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Amer. Petrol. Instit. Research Project 44, Carnegie Press, Carnegie Inst. of Technol., Pittsburgh, 1953.
14. American Chemical Society, "Physical Properties of Chemical Compounds," Volumes I and II, Advances in Chemistry Series #15 and 22, Amer. Chem. Soc., Washington, D. C. 1955, 1959.

Table I - Freezing Point Data - n-Alkanes in Isopar-M

n-Alkane	Heat of Fusion ΔH_m (Kcal/Mole)		Entropy of Fusion ΔS_m (Cal/Mol-deg.)		Freezing Point* $T_{m,o}$ ($^{\circ}$ K)	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
C-12	8.8	8.80	33.1	33.4	266	264
C-13	8.9	6.81	33.4	25.4	267	268
C-14	10.5	10.77	37.3	38.6	280	279
C-15	11.4	8.27	40.5	29.2	281	283
C-16	12.7	12.75	43.7	43.8	291	291
C-17	13.2	9.68	44.6	32.8	296	295

* - Extrapolated to 100%

Table II - Composition of Mixed Solvent (% w/w)

Solution	Isopar-M	Decalin	Tetralin	Butyl Benzene		
				(normal)	(secondary)	(tertiary)
A	40	40	-	-	20	-
B	40	40	20	-	-	-
C	80	-	20	-	-	-
D	80	-	-	-	20	-
E	80	-	-	6.7	6.7	6.7
F	50	25	-	-	-	25
G	-	-	-	33.3	33.3	33.3

Table III - Freezing Point Data - Solvent Effect

Solute	Solvent	Heat of Fusion, ΔH_f (Kcal/Mole) [†]	Entropy of Fusion, ΔS_f (Cal/Mole-Deg)	Freezing Point* $T_{m,0}$ (°K)
$n-C_{14}H_{30}$	$n-C_7H_{16}$	9.3	32.8	283
"	Isopar-M	10.5	37.3	280
"	sec-Butyl Benzene	11.3	39.0	291
"	(Liter.)	10.77	38.6	279
$n-C_{16}H_{34}$	$n-C_7H_{16}$	11.2	37.9	295
"	Decalin	11.9	41.3	289
"	Isopar-M	12.7	43.7	291
"	sec-Butyl Benzene	14.3	47.8	300
"	(Liter.)	12.75	43.8	291
"	Solution A	12.0	41.2	291
"	" B	12.4	42.6	290
"	" C	12.4	42.4	292
"	" D	12.6	42.8	294
"	" E	12.7	43.1	294
"	" F	12.7	43.4	293
"	" G	13.3	44.7	298
Naphthalene	sec-Butyl Benzene	3.9	10.4	374
"	Isopar-M	4.7	11.4	413
"	(Liter.)	4.32	12.21	354

* - Extrapolated to 100%

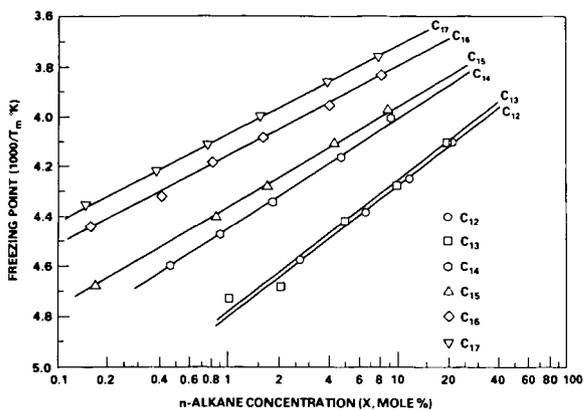


Figure 1 — Freezing Point vs Concentration — *n*-Alkanes in Isopar-M

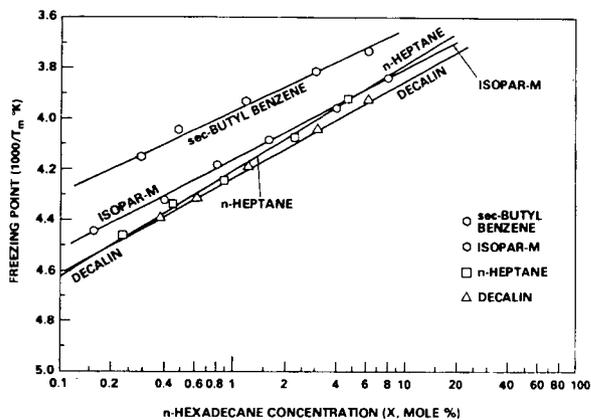


Figure 2 — Freezing Point vs Concentration — *n*-Hexadecane in Several Solvents

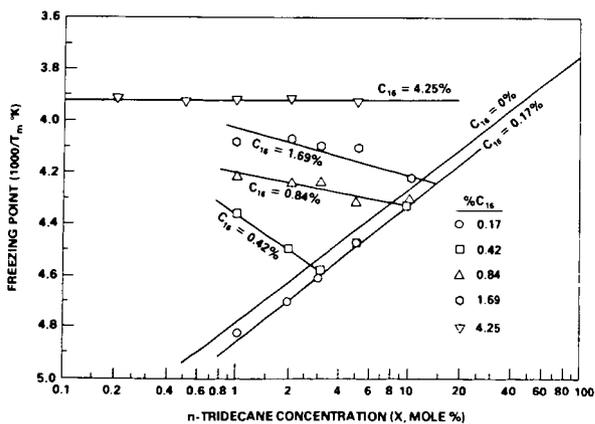


Figure 3 — Freezing Point vs *n*-Tridecane Concentration — *n*-Tridecane + *n*-Hexadecane in Isopar-M