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MELTING POINT AND VISCOSITY BEHAVIOR OF
HIGH ENERGY DENSITY MISSILE FUELS

Vitreous State Laboratory
Catholic University of America
Washington DC 20064

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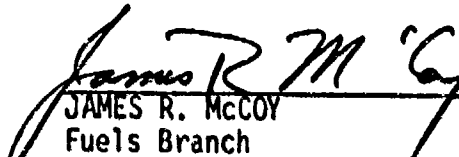
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This technical report has been reviewed and is approved for publication.


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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Three isomers of perhydrodi- (norbornadiene) (PHDNBD or RJ-5), the main component of RJ-5 and RJ-6 missile fuels, have been purified by recrystallizing the synthetic isomeric blends from acetone at dry ice temperature. The isomers have been designated HNN, HXX and Isomer I. HNN and HXX could be purified to 99.9% in three recrystallizations, but only 97% was reached with isomer I after thirteen recrystallizations. Melting points were measured by ASTM method D2386-67 as a function of composition for mixtures of the three RJ-5 isomers with themselves and with exo-		

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tetrahydrodi(cyclopentadiene) (XTHDCPD or JP-10). HNN and HXX each have two crystalline forms. The solid-solid transitions between these two forms are sluggish, so that depending on thermal history or the type of crystal used to seed the melt, either form might crystallize and remelt on heating. Hence most melts containing HNN and HXX as the main component could exhibit either of two melting points.

Enthalpies of fusion and solid and liquid heat capacities were measured by DSC for HNN and HXX. This allowed calculation of the ideal solution m.p. curves as a function of composition for melts in which HNN and HXX freeze out. The calculated ideal solution m.p. curves were in good agreement with the experimental data for the high m.p. forms of these two isomers, but the m.p. curves for the low m.p. forms disagreed with the ideal solution predictions, suggesting solid solution formation on crystallization. The experimental m.p. curves for the binary isomer I - XTHDCPD system could be used to predict m.p.'s for mixtures of isomer I also containing HNN. Hence data is now available to predict reliably the m.p. of the highest melting component, i.e., the liquidus temperature, of any fuel blend of HNN, HXX, isomer I and XTHDCPD of known composition. It was found that the maximum m.p. specification of -54°C for RJ-6 missile fuel (an RJ-5-JP-10 blend containing 36-42 wt% JP-10) could be met provided two or three of the RJ-5 isomers studied were present in appropriate amounts.

Shear viscosities and densities were measured as a function of temperature (-55 to 50°C) and composition for mixtures of HNN, HXX and isomer I with XTHDCPD. There was very little difference among the viscosity-composition isotherms for the three RJ-5 isomers. Depending on the RJ-5 isomer, blends containing 36-40 wt% or greater XTHDCPD will meet the ≤ 4 P at -54°C viscosity specification for RJ-6 fuel.

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I. INTRODUCTION

The research described here was carried out in an effort to understand the factors controlling freezing points and viscosities of high energy density missile fuels based on perhydrodi(norbornadiene) (PHDNBD). Several isomeric forms of PHDNBD exist; the usual formula is $C_{14}H_{18}$. Probable structures of these isomers along with their acronyms (HNN, isomer I, etc.) are shown in Fig. 1.* The military designation for the fuel consisting solely of PHDNBD isomers is RJ-5^{1,2}. Exo-tetrahydrodi(cyclopentadiene) (XTHDCPD, military designation JP-10, formula $C_{10}H_{16}$, structure shown in Fig. 1) is employed as a viscosity and melting point lowering diluent for RJ-5. An RJ-5 - JP-10 mixture with 36-42 wt% JP-10 is referred to as RJ-6^{1,2}.

Proposed military specifications^{1,2} call for a maximum melting point (i.e., equilibrium freezing point) of -54°C and a maximum kinematic viscosity of 400 cSt (approximately 4 P shear viscosity) at -54°C for RJ-6 fuel. Melting point and viscosity of RJ-5 - JP-10 blends depend on composition. In our study we have measured these two quantities along with the density for mixtures of three highly pure RJ-5 isomers - HNN, HXX and isomer I - with themselves and with JP-10. In addition, melting points (m.p.) have been measured for a large number of fuel blends prepared from "as synthesized" RJ-5 samples. Finally, heats of fusion and liquid and crystal heat capacities of two of the RJ-5 isomers - HNN

*Figures and tables are located at end of report.

and HXX - have been determined to allow calculation and comparison of ideal solution melting point - composition curves with those measured experimentally.

II. EXPERIMENTAL PROCEDURES

Chemical synthesis of RJ-5 gives a mixture of many isomers. Depending on synthesis conditions, one of these isomers will be the predominant form. Three different types of "as synthesized" RJ-5 in which the main isomeric constituents were respectively HNN (93%), HXX (75%) and isomer I (57%) were obtained from Suntech, Inc. The main isomeric constituent of each fuel was isolated by us by recrystallizing it from acetone at dry ice temperature. HNN and HXX could be purified to 99.9% (as determined by gas chromatography (GC)) in three recrystallizations, but thirteen recrystallizations of isomer I give a purity of only 97%. A few hundred mL of each isomer were purified to these levels and used for subsequent experiments. The XTHDCPD (JP-10) blended with these purified RJ-5 isomers was obtained from Suntech, Inc. in a purity of 99.9%. Samples for m.p. studies on fuel blends prepared from "as synthesized" RJ-5 were obtained from Wright-Patterson APB or from Suntech, Inc. All blends were prepared by weight from the component liquids.

Melting points were measured by ASTM method D2386-67³ using a calibrated thermocouple as a temperature sensor. The apparatus is shown in Fig. 2. In this technique about 10 mL of liquid sample are cooled in the air-jacketed test tube until it crystallizes. It is then reheated while stirring, and the temperature at which the last amount of crystal is observed visually to melt (or dissolve) is recorded as the m.p.. A liquid will generally supercool well below the equilibrium m.p. before crystallization commences. Measurement of the melting point rather than the freezing point ensures determination of the highest temperature at which the crystalline form of

the fuel can exist in equilibrium with the liquid.

All of the liquids studied here showed a strong tendency to supercool. Often there was considerable difficulty in inducing them to crystallize prior to measuring the m.p., particularly with those liquids blended from "as synthesized" RJ-5. The m.p. of pure JP-10 lies far below the temperature range of this study⁴, so that in all cases the only crystalline phases observed were those of the RJ-5 isomers. It was frequently found that a fuel needed to be thermally cycled below the m.p. for extended periods of time and seeded with a crystal of pure RJ-5 isomer to induce nucleation and growth of crystals. There were also on occasion some problems associated with accurately pinpointing the m.p. on reheating the crystallized samples. Water droplets or ice crystals either from moisture initially dissolved in the fuel or from moisture condensed into the fuel from the atmosphere at low temperatures while crystallizing the sample could give the fuel a cloudy appearance and obscure the m.p.. The remedies here were respectively to dry the fuel for 24 hours over a molecular sieve and filter it before starting the m.p. determination and to keep a dry N₂ blanket over the fuel during the m.p. determination. The presence of bubbles introduced by stirring of the viscous, cold fuel sample could also obscure the m.p.; here the best solution was to illuminate the sample strongly from behind.

Enthalpies of fusion and heat capacities of crystals below the m.p. and liquid above the m.p. were measured with a Perkin-Elmer Model DSC-2 differential scanning calorimeter (DSC). Accurate heat of fusion measurements can only be obtained on high purity compounds, since impure compounds melt over a wide range of temperature, giving rise to problems in accurate measurement of the heat absorbed during melting⁴. Hence these measurements were carried out only for the HNN and HXX RJ-5 isomers, which had been purified to the 99.9% level.

Liquid kinematic viscosities ν were measured using factory calibrated Ubbelohde capillary viscometers from the Cannon Instrument Company. Densities D were measured to an accuracy of 0.1% using a dilatometer of about 10 mL volume. Shear viscosity η is given by the νD product and is estimated to be accurate to about 0.5%. Viscosity and density measurements were carried out from 50°C down to either about -55°C or a temperature just above that where the liquid crystallized. Due to supercooling it was possible in all cases to determine η and D for the liquids down to temperatures well below their equilibrium m.p.'s. During measurements viscometers and dilatometers were thermostated in regulated liquid baths (water above room temperature, methanol below room temperature); bath temperatures were measured to an accuracy of 0.05°C using a copper-constantan thermocouple which had been calibrated against an NBS-certified Pt resistance thermometer.

III. RESULTS AND DISCUSSION

A. Melting Point-Composition Plots

Plots of m.p., T_m , versus composition, X_i , of component i in mole fraction* for solutions of the highly purified RJ-5 isomers with one another and with XTHDCPD are shown in Figs. 3-9. The numerical T_m - X_i data are given in Table I. The accuracy and reproducibility of the m.p.'s were about $\pm 0.3^\circ\text{C}$ in most cases. The uncertainty became somewhat larger for fuel samples melting at the lowest temperature in each of the systems studied, but in no case was greater than $\pm 1.1^\circ\text{C}$.

*Mole fraction X_i is related to weight fraction w_i by the expression

$$X_i = (w_i/M_i) / \sum (w_k/M_k)$$

where M_i is the molecular weight of component i and the sum in the denominator is taken over all components. For mixtures containing only RJ-5 isomers $X_i = w_i$, while for mixtures containing XTHDCPD X_i of an RJ-5 isomer is somewhat less than w_i .

One of the most remarkable findings of the study was the observation of two distinct m.p.'s for the HNN and HXX isomers (cf. Figs. 3, 4 and 6). This was first detected in measuring the m.p. of pure HNN, where it was found that about half the time the sample would melt at 0.5°C and the other half at 7.5°C. With the HXX isomer, if the m.p. was measured immediately after crystallization it was found to be 11.3°C, while if the crystallized sample was held for 1 to 2 hours near dry ice temperature it was found to be 17.0°C. The explanation for this phenomenon is that there are two crystalline forms or polymorphs of the HNN and of the HXX isomers, which we will designate respectively as "low m.p." and "high m.p.". (Rhombic and monoclinic sulfur are an inorganic example of this sort of phenomenon.) It can be shown from thermodynamics that in the vicinity of the lower m.p. the low m.p. form is metastable with respect to the high m.p. form. Hence if the low m.p. polymorph were initially formed on crystallization and if the system followed the path of lowest free energy during subsequent heating, the low m.p. form should convert via a solid-solid transition into the high m.p. form before melting takes place. Such solid-solid transitions are frequently kinetically impeded and sluggish, as was certainly the case here with the HNN and HXX isomers, allowing the low m.p. form to melt without ever passing through the high m.p. crystalline form.

By crystallizing a sample of pure HNN and HXX, allowing it to melt partially, measuring the temperature at which this occurred, and then recooling the sample before melting was complete, we were able to produce crystalline samples which were known to be either low m.p. or high m.p. polymorph. These samples were used for heat of fusion and heat capacity determinations on pure HNN and HXX, as well as for seeding fuel mixtures containing HNN and HXX in m.p. determinations.

Only one m.p. was observed for the high purity (97%) PHDNBD isomer I. It is not known whether isomer I has only one crystalline form or whether it has a low m.p. polymorph which converts readily to the high m.p. polymorph prior to melting.

Both the low m.p. and high m.p. polymorphs of HXX and HNN could crystallize from solutions as well as from the pure liquids, so that two plots of T_m vs. X_i could be observed experimentally, one for the low m.p. and one for the high m.p. form (cf. Figs. 3, 4 and 6). For the solution we usually found that if the liquid were allowed to crystallize without seeding, the low m.p. form would crystallize out and subsequently melt on reheating. In order to crystallize and observe the m.p. for the high m.p. polymorph, it was necessary to seed the solution with a small crystal of the pure high m.p. form. In Figs. 3-9 and in Table I we have indicated clearly that for each T_m value whether or not the solution was seeded to nucleate a particular crystal phase, and if so, what seed crystal was used. In some systems containing HNN and HXX (Figs. 3, 4 and 6) we determined the T_m vs. X_i curves for both the low m.p. and high m.p. forms. In other systems, however, we determined the curves for only the high m.p. form (Figs. 7-9). This was because in setting a maximum m.p. specification for a particular fuel blend, only the T_m value for melting of the high m.p. polymorph is of interest.

For solutions containing two different RJ-5 isomers different m.p.'s could be observed near the minimum in the T_m vs. X_i curves by seeding the solution so as to crystallize one or the other of the isomers. For example, at the 0.50 mole fraction composition of the HNN-isomer I T_m vs. X_i plot of Fig. 7 seeding with isomer I crystals leads to crystallization of only isomer I, which melts at -31.7°C . Seeding with high m.p. HNN crystals

causes crystallization of only high m.p. HNN, which melts at -19.5°C .

In Fig. 10 is shown a plot of T_m versus mole fraction HNN for blends prepared from "as synthesized" RJ-5 samples. Open data points refer to blends containing only RJ-5 isomers, while filled data points are for blends of RJ-5 with JP-10 or with JP-10 plus RJ-4. (RJ-4 is a mixture of isomers of tetrahydrodi(methylcyclopentadiene)¹). All of the fuels in Fig. 10 contained at least moderate amounts of HNN and were seeded with high m.p. HNN crystals, so that it is the high m.p. HNN which crystallized from and subsequently melted in these samples. The HNN mole fraction was obtained from GC analysis of the blend or its component liquids. Scatter of the data in Fig. 9 is probably due more to uncertainties in composition than to uncertainties in the T_m measurement.

B. Heats of Fusion, Heat Capacities and Solid-Solid Transition Temperatures

In Table II are listed the molar enthalpies or heats of fusion, $\Delta\bar{H}_{f,i}$, of pure low m.p. and high m.p. HNN and HXX, along with the m.p.'s $T_{m,i}^0$ determined by the ASTM method. The $\Delta\bar{H}_{f,i}$ values are averages of between 2 and 13 DSC measurements carried out at a heating rate of 0.625 K/min on each crystal, and the uncertainties given in Table I are the standard deviations from the mean. These latter values suggest an accuracy of roughly 2% for the $\Delta\bar{H}_{f,i}$ values.

Heat capacities C_p were measured at a DSC heating rate of 5 K/min over moderate temperature ranges ($\sim 40^{\circ}\text{C}$) below or above the m.p. for, respectively, high m.p. crystal and liquid HNN and HXX. C_p was found to be a linear function of temperature over this range, and the experimental results are given in Table III in equation form:

$$C_p(\text{cal/g } ^{\circ}\text{C}) = a + bT(^{\circ}\text{C}) \quad (1)$$

The a and b terms were obtained from a linear fit to the combined data from between three and eight DSC scans for each material. The standard deviations from the least squares fits indicate an accuracy of 1-2% for the heat capacity results.

Heat of fusion and heat capacity results were reported previously⁴ for impure samples of HNN (96.8% by GC) and HXX (98.6% by GC). In this prior study we were unaware of the existence of two crystalline polymorphs of these compounds, and heat of fusion and crystal heat capacity were measured for whatever crystalline phase formed on cooling a small sample on the DSC. Comparison of the m.p.'s in Table II with those previously⁴ (280.7 vs. 281.0 K for HNN, 284.5 vs. 285.3 K for HXX) indicates that in the previous study high m.p. HNN and low m.p. HXX were formed. The heats of fusion for these crystalline forms in the previous study were about 42% higher for HNN and 17% higher for HXX than those of Table II. The discrepancies are undoubtedly due to the problems, mentioned earlier, of obtaining accurate values on the impure samples of the previous study.

Heat capacity results are much less sensitive to impurities than heat of fusion results, and the C_p values of the previous and present studies agree within experimental error for high m.p. HNN crystal and HNN and HXX liquids. The C_p values for low m.p. HXX (previous study) and high m.p. HXX (present study) are also in agreement within experimental error, indicating very little difference in C_p between the two HXX polymorphs. This is probably not surprising in view of the small enthalpy difference between the two crystalline phases.

Although we were unable to observe the solid-solid transition between the low and high m.p. forms of HNN and HXX, we can calculate the temperature, T_{ss} , of this transition from the data in Table II. At T_{ss} the two crystalline forms have the same Gibbs free energy, and it follows from simple

thermodynamics that

$$T_{ss} = \frac{\Delta \bar{H}_{f,2} - \Delta \bar{H}_{f,1}}{(\Delta \bar{H}_{f,2}/T_{m,2}^0) - (\Delta \bar{H}_{f,1}/T_{m,1}^0)} \quad (2)$$

where subscripts "1" and "2" refer respectively to the low and high m.p. polymorphs and temperatures must be expressed in kelvins.

For HNN Eq. (2) gives a value of 289.4 ± 2.0 K ($16.2 \pm 2.0^\circ\text{C}$) for T_{ss} , where the probable error in T_{ss} was calculated by assuming that the errors in the various quantities which appear in Eq. (2) ($\Delta \bar{H}_{f,2}$, $T_{m,2}^0$, etc.) were equal to the standard deviations in Table II. T_{ss} thus lies above T_m for both low and high m.p. HNN. Hence the low m.p. polymorph is metastable (at atmospheric pressure) with respect to the high m.p. form at all temperatures below either m.p.. A pair of polymorphs with this property are known as monotropes.⁵

For HXX Eq. (2) gives a value of 240 ± 19 K ($-33 \pm 19^\circ\text{C}$) for T_{ss} . The uncertainty in T_{ss} for HXX is rather large because the $\Delta \bar{H}_{f,i}$ values for the two polymorphs are close in value, giving rise to a small difference between large terms in both numerator and denominator of Eq. (2). In any event, T_{ss} for HXX appears to lie below the m.p. of either crystalline form; a pair of polymorphs with this property are known as enantiotropes.⁵ Below T_{ss} the enantiotrope of lower m.p. is the more thermodynamically stable form, while above T_{ss} the high m.p. form is the more stable. In view of the transformation from low to high m.p. HXX which takes place when the crystallized sample is held not far from dry ice temperature, it seems likely that the lower limit for T_{ss} is probably closest to the actual value.

C. Calculation of Ideal Solution m.p. vs. Composition Plots

The m.p. $T_{m,i}$ for component i present in solution at mole fraction X_i can be calculated using thermodynamic fusion data of the type given in Table II via the equation⁶:

$$\begin{aligned} \ln X_i = & (\Delta \bar{H}_{f,i}/R) [(1/T_{m,i}^O) - (1/T_{m,i})] \\ & - (\Delta \bar{C}_{p,i}/R) [1 - (T_{m,i}^O/T_{m,i}) + \ln(T_{m,i}^O/T_{m,i})] \end{aligned} \quad (3)$$

where $\Delta \bar{C}_{p,i}$ is the difference between liquid and crystal heat capacity per mole at the m.p. of pure i , R is the ideal gas constant and temperatures are in kelvins. The first term on the right side (containing $\Delta \bar{H}_{f,i}$) expresses the major dependence of $T_{m,i}$ on X_i , while the second term (containing $\Delta \bar{C}_{p,i}$) is a relatively minor correction to the first term for the temperature dependence of the heat of fusion.

Equation (3), which will be referred to as the "ideal solution m.p. equation", is valid under two conditions. (A) The liquid solution of the components i is ideal, that is, there is no heat of mixing of the pure liquids, so that the activity coefficients are unity for all components. (B) Component i freezes out of solution as the pure crystal, that is, there is no solid solution or compound formation on freezing. Deviations of experimental $T_{m,i}$ vs. X_i curves from the predictions of Eq. (3) are a measure of the extent to which either or both of these conditions are violated. Condition (A) is expected to be satisfied to a good approximation for solutions of PHDNBD isomers with themselves and with XTHDCPD, since all these molecules are polycyclic saturated hydrocarbons of comparable shape and size. With regard to condition (B), no compound formation is expected on crystallization because of the weak intermolecular forces between these

molecules. Whether or not solid solutions are formed, however, is a matter for experimental verification, e.g., whether or not the predictions of Eq. (3) agree with the data.

Note that Eq. (3) predicts that the m.p. of component i in solution depends only on its concentration X_i and is independent of the identity of the other solution components. Note also that, provided the relevant thermodynamic data are available, Eq. (3) can be used to predict the m.p. of each different component i of the solution and, if component i has more than one crystalline polymorph, the m.p. of each polymorph. These $T_{m,i}$'s will in general be different for different components or for polymorphs of the same component.

$T_{m,i}$ versus X_i has been calculated from Eq. (3) for high m.p. HNN and HXX using the data in Table II. ($\Delta\bar{C}_{p,i}$ values given in Table II were obtained from the data in Table III.) These are shown as solid lines (labelled "ideal sol'n") in Figs. 3, 4 and 6-10. In general the agreement between the ideal solution curves and the experimental data is quite good for high m.p. HNN and HXX, showing that in general freezing of high m.p. HNN and HXX from solutions containing other PHDNBD isomers and/or XTHDCPD fulfills the conditions for the validity of Eq. (3).

Equation (3) does not in general give a good prediction of $T_{m,i}$ vs. X_i for low m.p. HNN and HXX. This is shown, for instance, in Fig. 3 for HNN, where the ideal solution curve calculated for low m.p. HNN freezing from solutions with XTHDCPD lies well below the experimental curve. The deviation of the experimental from the calculated curve in this case suggests that low m.p. HNN forms solid solutions with XTHDCPD on freezing.⁶ The $T_{m,i}$ vs. X_i curve in Fig. 6 for low m.p. HXX freezing out of solutions with HNN shows a distinct shoulder at $X_{\text{HXX}} = 0.95$. This type of curve is expected for

solid solution formation with a solubility limit of the minor component (HNN) in the solid solution.⁶ Since, as mentioned before, we are interested here in fixing the maximum melting points for these fuels, the subsequent discussion of the $T_{m,i}$ vs. X_i curves for HNN and HXX will be limited to those for the high m.p. polymorphs, for which Eq. (3) seems to be valid.

Since the heat of fusion data are lacking for isomer I, no ideal $T_{m,i}$ vs. X_i curve could be predicted for this PHDNBD compound. However it was found experimentally that the $T_{m,i}$ vs. X_i curves for isomer I were, within experimental uncertainty, the same whatever other components were present in the solution. This is shown in Fig. 5, where a smooth curve (large dashes) drawn through the data for the isomer I-XTHDCPD system is compared with the smooth curve (small dashes) drawn through the data of Fig. 7 for the isomer I-HNN system. Similarly, the dashed line for the isomer I m.p. curve of Fig. 8 is taken from Fig. 5 and agrees well with the experimental data. Since an absence of dependence of the $T_{m,i}$ vs. X_i curves on the nature of the other components is a criterion for ideal solution behavior, it is safe to conclude that the solutions containing isomer I are also ideal.

Equation (3) predicts a phase diagram of the simple eutectic type for binary systems.^{5,6} $T_{m,i}$ for each component should decrease as the concentration of the other component increases, and the two $T_{m,i}$ vs. X_i curves should intersect at a point called the eutectic temperature and composition. At the eutectic composition the liquidus temperature, i.e., the maximum temperature at which a crystalline phase can exist at equilibrium, is a minimum. The binary solution $T_{m,i}$ vs. X_i plots for high m.p. HNN, high m.p. HXX and isomer I of Figs. 6 and 7 exhibit this minimum in liquidus temperature at the eutectic. The same is true of the pseudobinary solution plots of Figs. 8 and 9 where XTHDCPD is a non-crystallizing diluent whose

mole fraction is kept constant at 0.50. There very likely is also a eutectic point in the PHDNBD-XTHDCPD binary solution $T_{m,i}$ vs. X_i curves for isomer I and high m.p. HNN or HXX. Because pure XTHDCPD has a very low m.p., however, these eutectic points would be expected to occur at temperatures well below the temperature range of this study and at compositions very close to pure XTHDCPD. Consequently the PHDNBD-XTHDCPD eutectics are not observable in Figs. 3-5.

D. Estimation of m.p.'s for RJ-5 - JP-10 Blends

The ideal solution curves of Figs. 3-5 can be used to estimate m.p.'s of RJ-5 - JP-10 blends from their compositions (obtained, e.g., from GC) and vice versa. Note that we are interested in maximum m.p.'s, so that one wants to use the HNN and HXX $T_{m,i}$ curves for the high m.p. polymorphs. Also, the problem must be solved using mole fraction composition units. A couple of examples should serve to illustrate the method.

Example A: What is the maximum m.p. of an RJ-6 fuel containing 38 wt% JP-10 and 62 wt% Shelldyne-H?

Shelldyne-H is an "as synthesized" RJ-5, containing about 70 wt% HNN isomer and smaller amounts of other PHDNBD isomers. These latter, since they are present in smaller amount, may be presumed to have lower $T_{m,i}$'s than HNN. We first convert to mole fraction units using the equation on p. 4 and the molecular weights of 136.2 and 186.3 g/mol for, respectively, XTHDCPD (JP-10) and PHDNBD:

$$X_{\text{HNN}} = \frac{(0.70)(62)/186.3}{62/186.3 + 38/136.2} = 0.38$$

From the ideal solution curve for high m.p. HNN in Fig. 3 we then find the maximum m.p., -30°C .

Example B: If the maximum m.p. of a fuel must not exceed -54°C , what are the maximum contents of HNN, HXX and isomer I?

From Figs. 3, 4 and 5 determine the mole fractions of the respective isomers for which $T_{m,i}$ is -54°C . These are

$$X_{\text{HNN}} = 0.18$$

$$X_{\text{HXX}} = 0.23$$

$$X_{\text{iso I}} = 0.33$$

An RJ-6 fuel containing 40 wt% JP-10 contains 0.48 mole fraction JP-10 and 0.52 mole fraction PHDNBD. Since the sum of the PHDNBD mole fractions calculated above is 0.74, there would be no difficulty in preparing an RJ-6 blend containing 40 wt% JP-10 using all three PHDNBD isomers and meeting a maximum m.p. specification of -54°C . In fact such an RJ-6 blend could be prepared using only HXX and isomer I and, very nearly, using only HNN and isomer I.

E. Viscosities and Densities

Densities of the purified liquid PHDNBD isomers and their mixtures with XTHDCPD were linear functions of temperature. Experimental results are given in Table IV. In Table V are given the parameters obtained from least squares fits to the equation:

$$D(\text{g/cm}^3) = D(0) - BT(^{\circ}\text{C}) \quad (4)$$

The densities measured here are in good agreement with the less accurate results reported previously⁴ for HNN, HXX and XTHDCPD.

Shear viscosity results are also listed in Table IV. The data for HNN, HXX, isomer I and XTHDCPD are shown in Fig. 11 in the form Arrhenius plots of $\log \eta$ vs. $1/T$. These plots are typical of those observed for nearly all liquids, namely, they are not linear, but curved

and concave upwards. It was found, as previously^{4,7}, that the temperature dependence of shear viscosity could be described within experimental error by the semi-empirical VTF equation:

$$\ln \eta(P) = A + B/(T(K) - T_0) \quad (5)$$

where A, B and T_0 are constants. Values of these parameters for each liquid studied were obtained by a least squares fit to the $\ln \eta$ vs. T data and are given in Table VI. These parameters can be used to interpolate viscosity for a given composition at temperatures within the experimental range and, with caution, to extrapolate viscosity values beyond the experimental temperature range. Shear viscosity values for HNN, HXX and XTHDCPD are in reasonable agreement with those reported previously^{4,7}. The biggest discrepancy is for XTHDCPD, where the previous results were several percent higher than the present results. This is undoubtedly because the previous XTHDCPD sample contained as an impurity about 4% of the endo isomer, which has a considerably higher viscosity than the exo isomer.

Shear viscosity isotherms of $\log \eta$ vs. mole fraction XTHDCPD for mixtures of each of the PHDNBD isomers with XTHDCPD are shown in Figs. 12 and 13 at four temperatures. The lines are smooth curves drawn through the data points; a dashed line indicates regions where the data points were extrapolated beyond the experimental temperature range via Eq. (5). The viscosity isotherms of Figs. 12 and 13 for the different PHDNBD isomers all lie very close to one another, so that at a given temperature η depends primarily on the XTHDCPD mole fraction. Isotherms such as those of Figs. 12 and 13 can be used to interpolate viscosity values at a given temperature and XTHDCPD mole fraction for a given PHDNBD isomer - XTHDCPD binary. For hydrocarbon liquids whose viscosity differences are small, logarithm of viscosity is generally linear in mole fraction composition⁷. Consequently, viscosities of PHDNBD - XTHDCPD mixtures containing more than two components

can be obtained by interpolation of the logarithm of the viscosity at constant temperature and mole fraction of XTHDCPD:

$$\ln \eta = (\sum X_i \ln \eta_i) / (1 - X_{\text{XTHDCPD}}) \quad (6)$$

where η_i is the viscosity of a PHDNBD - XTHDCPD binary solution at a given temperature and mole fraction XTHDCPD, and the sum is taken over only the PHDNBD components. For example, at -40°C $\ln \eta(\text{P}) = 0.698$ for 0.60 HNN - 0.40 XTHDCPD and $\ln \eta(\text{P}) = 0.527$ for 0.60 HXX - 0.40 XTHDCPD. Consequently at -40°C for 0.15 HNN - 0.45 HXX - 0.40 XTHDCPD:

$$\ln \eta(\text{P}) = [(0.15)(0.698) + (0.45)(0.527)] / [1 - 0.40] = 0.570$$

$$\eta = 1.77 \text{ P}$$

RJ-6 fuel must meet a maximum viscosity specification of 4P at -54°C . Depending on the PHDNBD isomer present, Fig. 13 indicates this is possible if X_{XTHDCPD} is, at a minimum, 0.43-0.48, that is, 36-40 wt% JP-10. Since the composition specification for RJ-6 fuel is 36-42 wt% JP-10, it appears that RJ-6 blends containing the three RJ-5 isomers studied here can be prepared to meet the viscosity specification, but just barely.

IV. CONCLUSIONS

We have elucidated via experiment the factors controlling melting points and shear viscosities of mixtures of three PHDNBD isomers with themselves and with XTHDCPD. The data can be used to estimate accurately m.p.'s and viscosities from a knowledge the composition of missile fuel blends containing these components. It appears that RJ-6 fuel blends containing 36-42 wt% XTHDCPD can be prepared to meet specifications of a maximum m.p. of -54°C and a maximum viscosity of 4P at -54°C .

Experimental certification of the maximum m.p. of an RJ-5 - JP-10 fuel blend presents difficulties. The blend is likely to be extremely difficult to crystallize without seeding. Even if crystallization does occur without seeding, the crystals formed may not be those of the isomer and polymorph with the maximum m.p. for that composition. Reliable certification of the maximum m.p. appears to require some prior knowledge of the composition and seeding with high m.p. crystals of the RJ-5 component judged most likely to have the maximum m.p.. For the near future, at least, small samples of purified HNN, HXX and isomer I for preparation of seed crystals for m.p. tests can be obtained from C. T. Moynihan at the Materials Engineering Department, Rensselaer Polytechnic Institute, Troy, NY 12181.

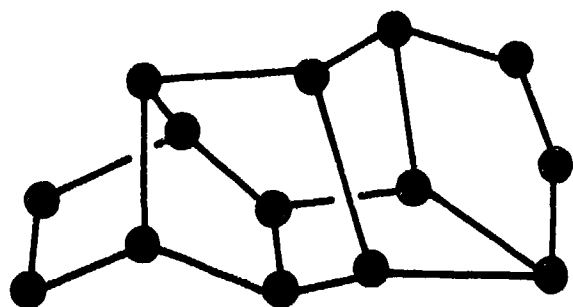
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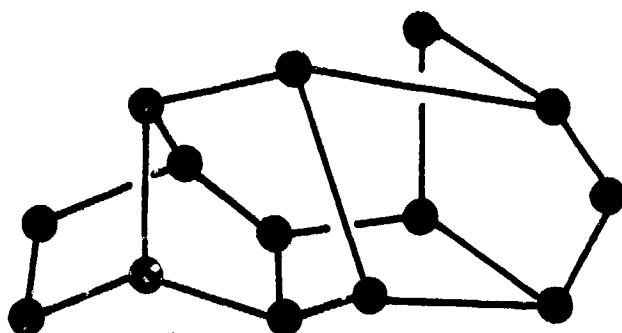
FIGURE CAPTIONS

- Figure 1. Structural formulae for RJ-5 isomers and for JP-10. Acronyms used in text: HXX = hexacyclic exo-exo-dihydrodi(norbornadiene); HNN = hexacyclic endo-endo-dihydrodi(norbornadiene); XTHDCPD = exo-tetrahydrodi(cyclopentadiene).
- Figure 2. Apparatus for m.p. determination.
- Figure 3. M.p. versus mole fraction HNN for HNN-XTHDCPD mixtures.
- Figure 4. M.p. versus mole fraction HXX for HXX-XTHDCPD mixtures.
- Figure 5. M.p. versus mole fraction isomer I for isomer I - XTHDCPD mixtures. Dashed line labelled "HNN-isomer I binary" is from Fig. 7.
- Figure 6. M.p. versus mole fraction HXX for HXX-HNN mixtures.
- Figure 7. M.p. versus mole fraction isomer I for HNN - isomer I mixtures.
- Figure 8. M.p. versus mole fraction HNN for pseudobinary HNN - isomer I mixtures containing a constant 50 mol % XTHDCPD.
- Figure 9. M.p. versus mole fraction HXX for pseudobinary HXX-HNN mixtures containing a constant 50 mol % XTHDCPD.
- Figure 10. M.p. versus mole fraction HNN for blends of "as-synthesized" missile fuels. All blends seeded with high m.p. HNN.
- Figure 11. Arrhenius plots of shear viscosity of HNN, HXX, isomer I and XTHDCPD.
- Figure 12. Shear viscosity isotherms at 0 and 50°C for binary mixtures of PHDNBD isomers with XTHDCPD.
- Figure 13. Shear viscosity isotherms at -54 and -40°C for binary mixtures of PHDNBD isomers with XTHDCPD. Dashed lines show regions where viscosity points were obtained by extrapolation beyond the experimental region using Eq. (5).

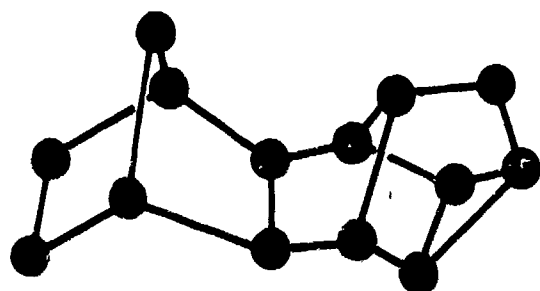
RJ-5 isomers



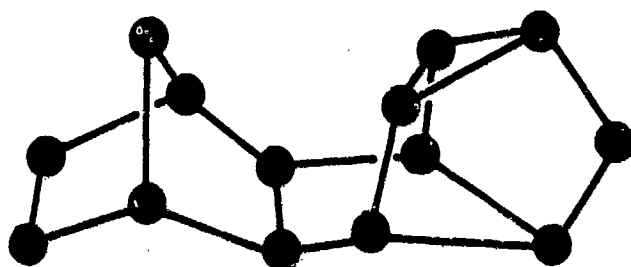
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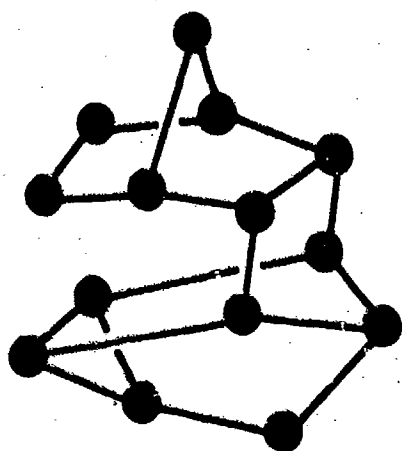
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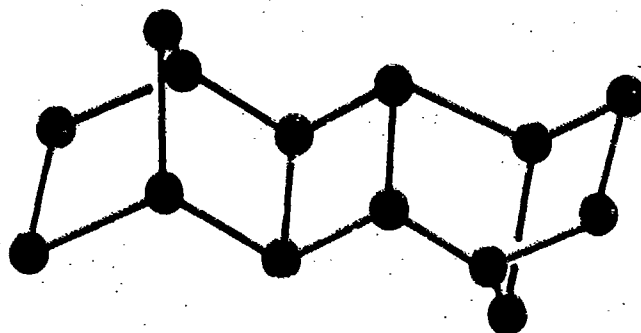
HXX



HXN

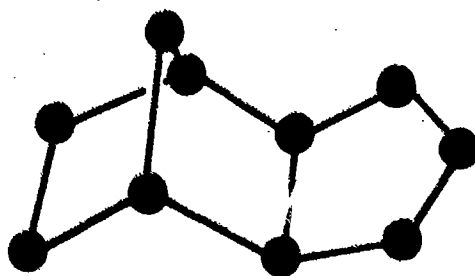


HNN



PXIX

Fig. 1.



XTHDCPD

= JP - 10

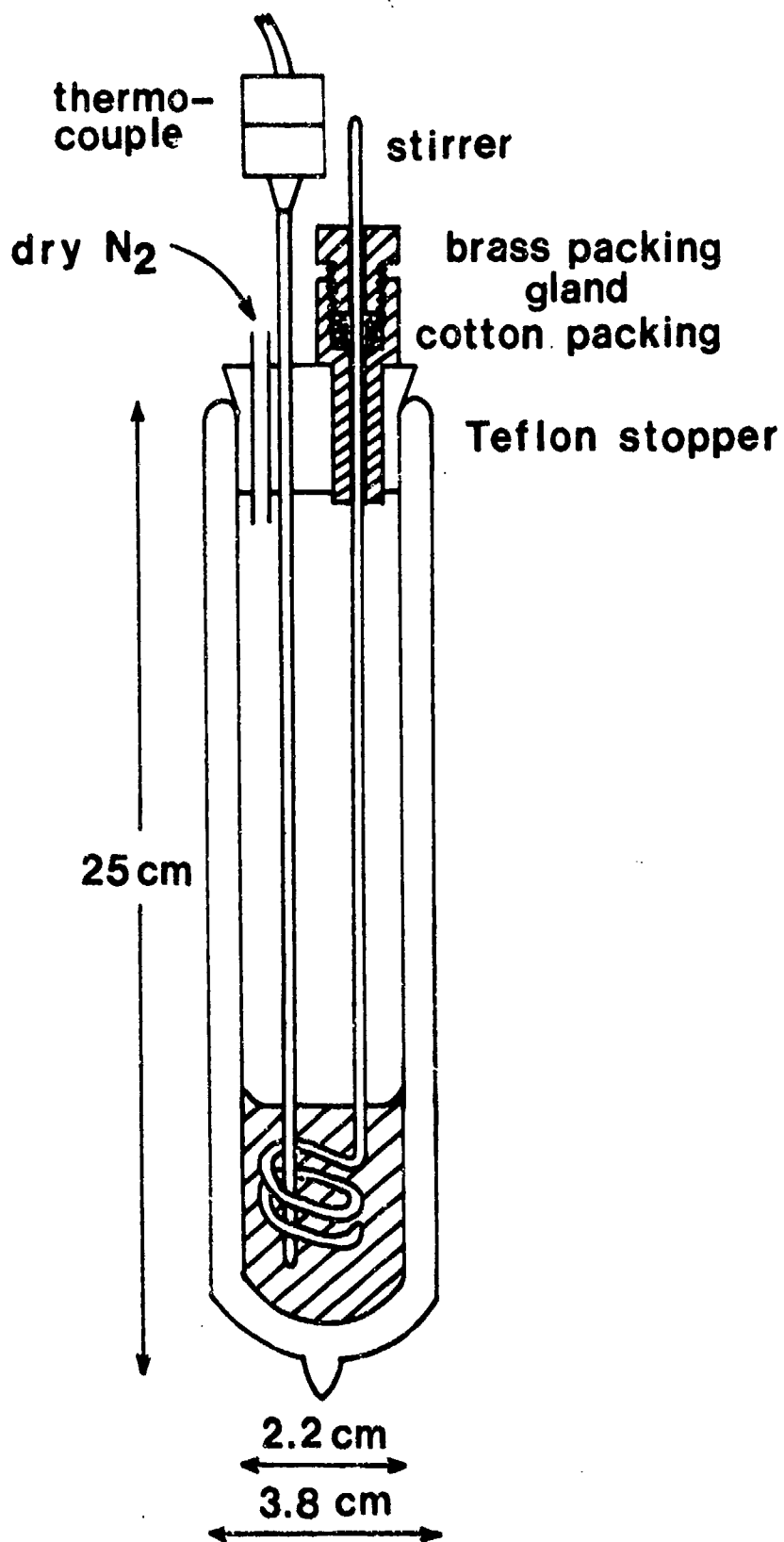


Fig. 2.

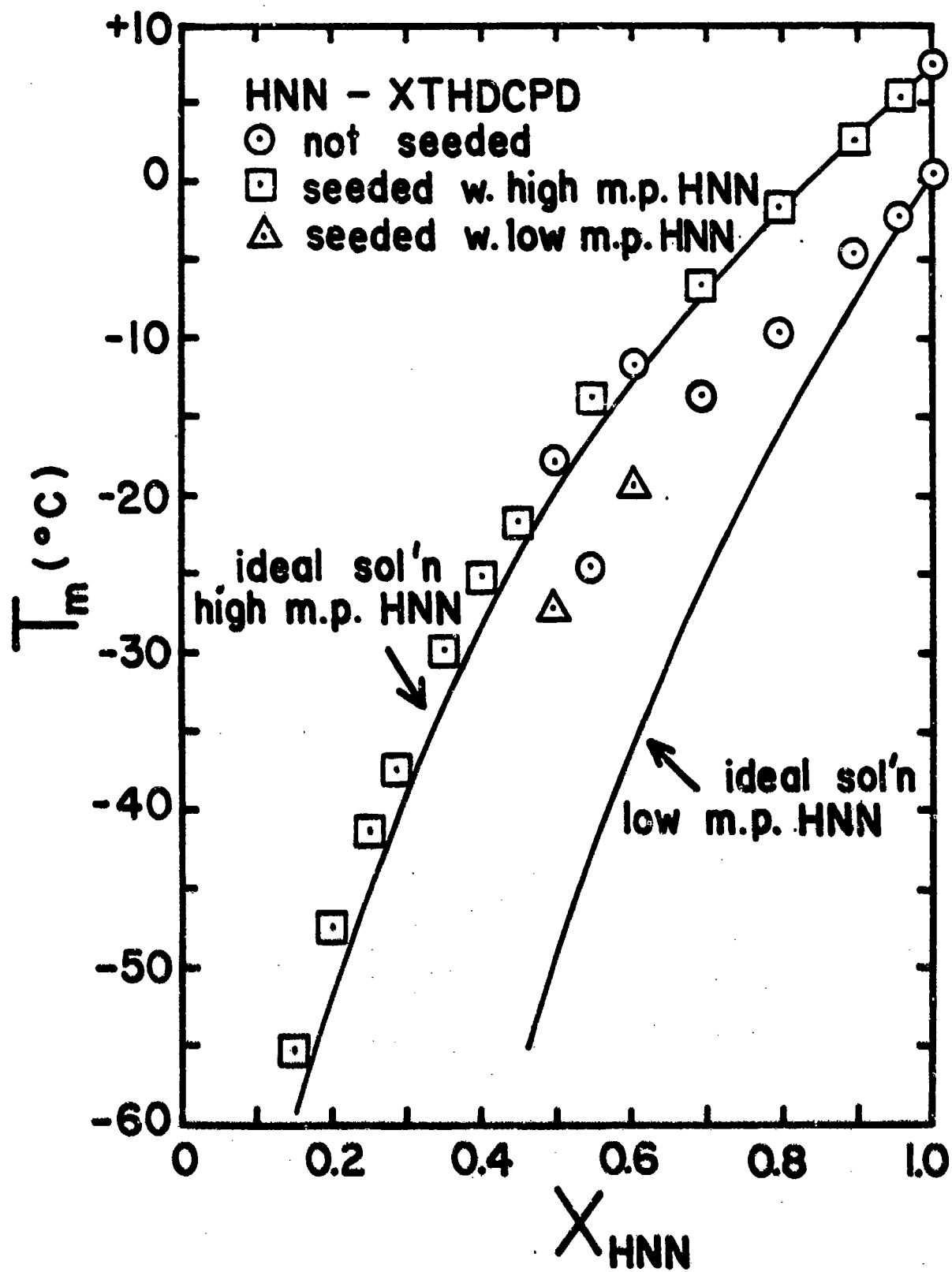


Fig. 3

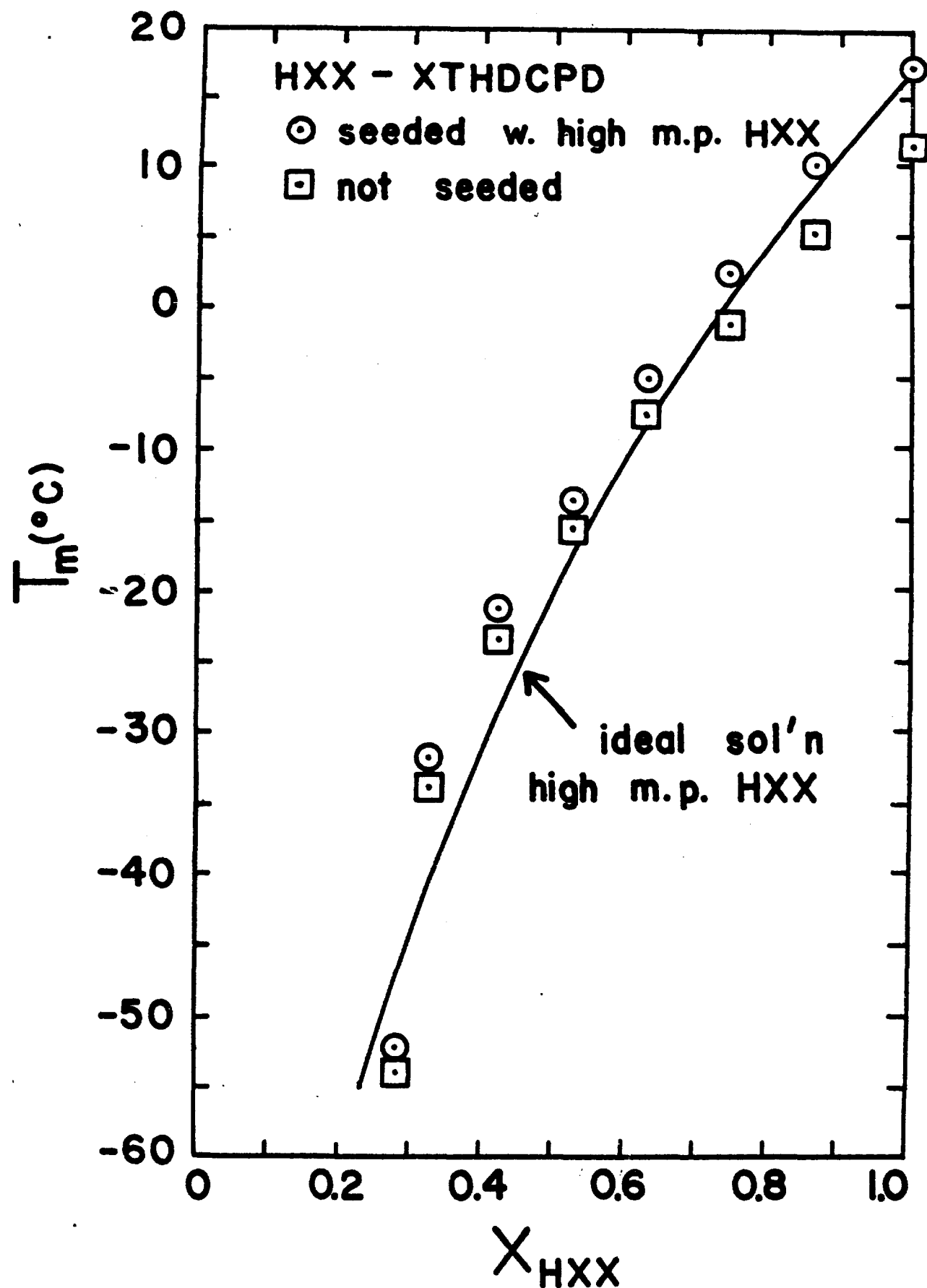


Fig. 4.

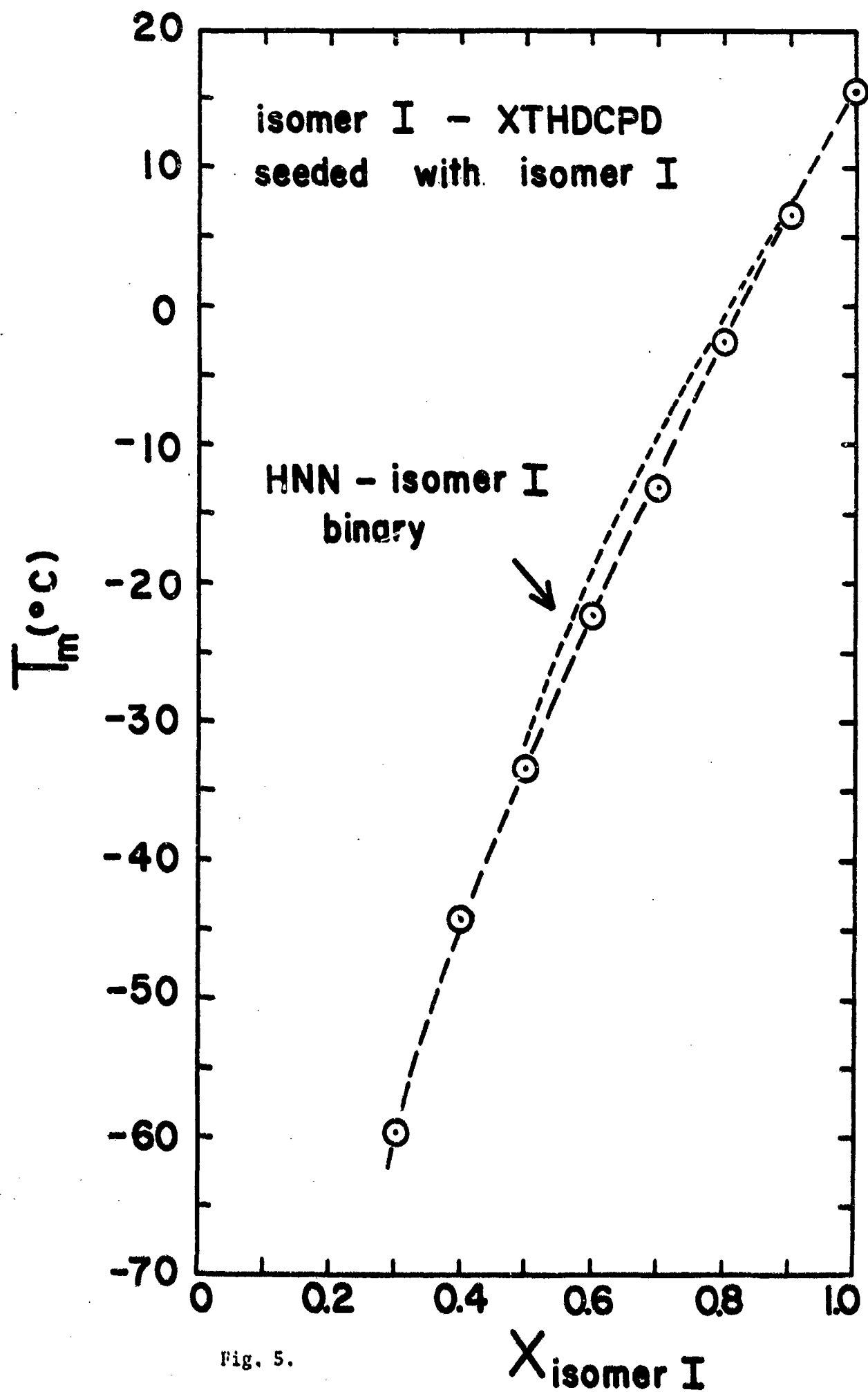


Fig. 5.

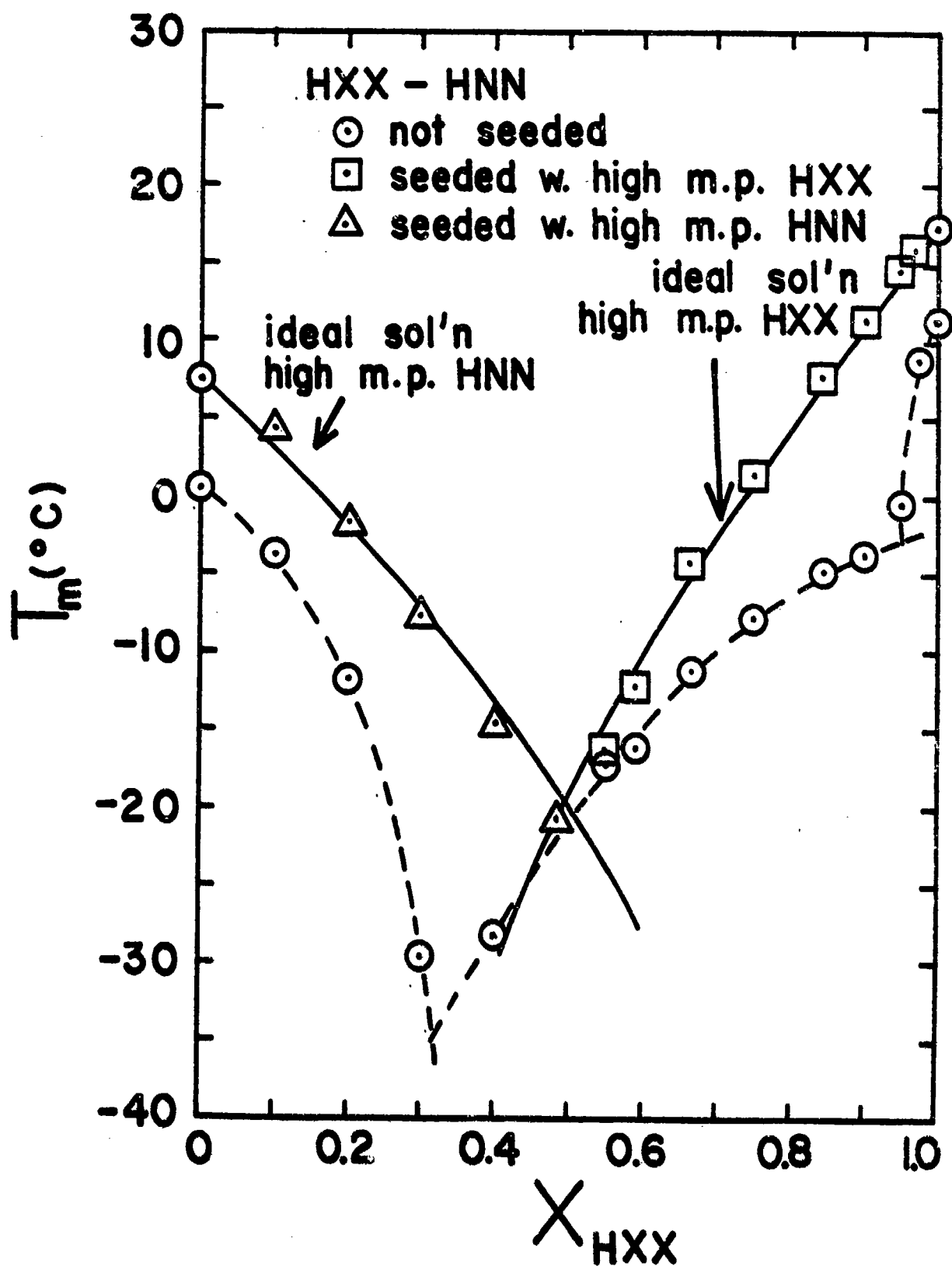


Fig. 6.

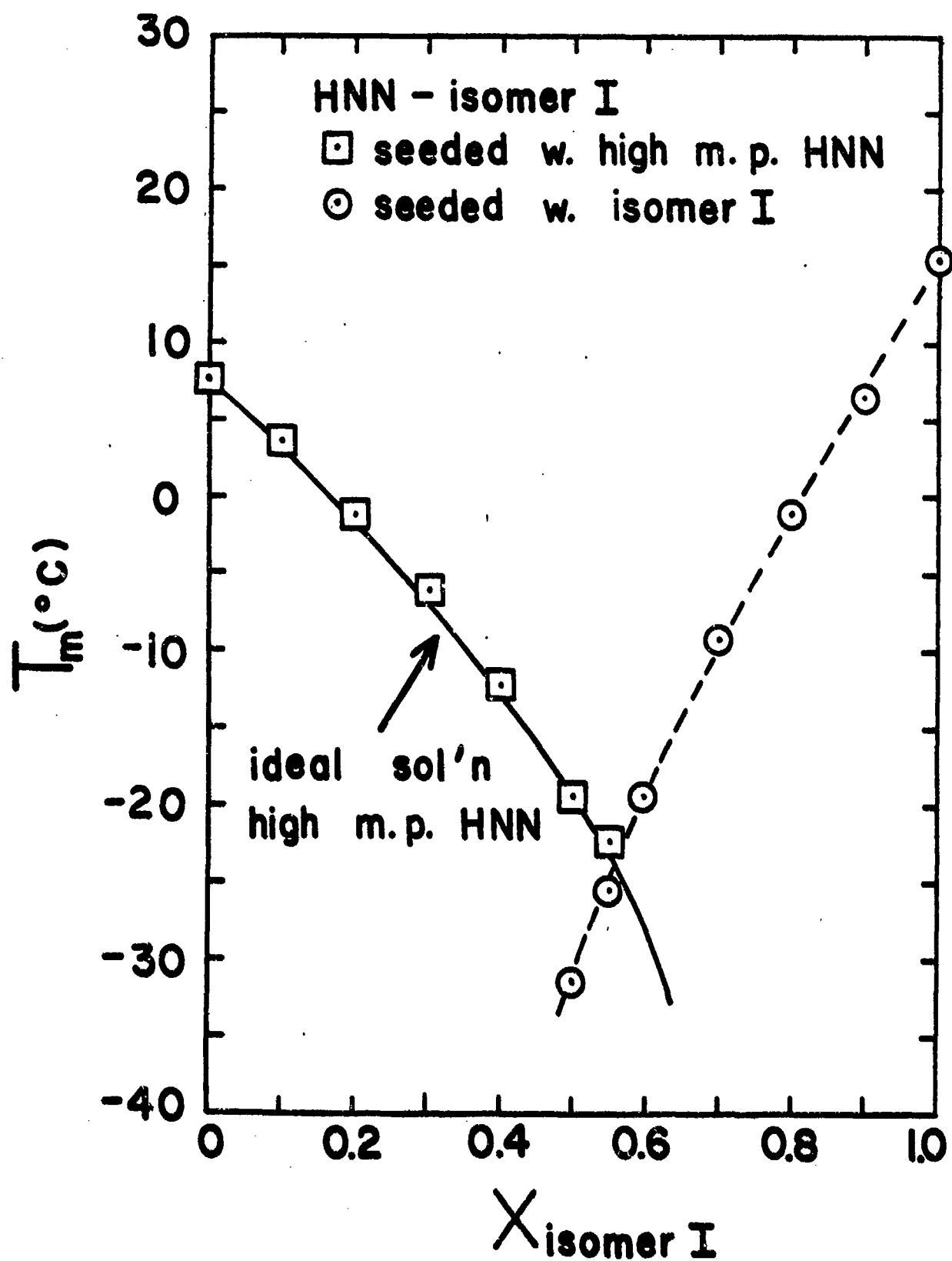


Fig. 7.

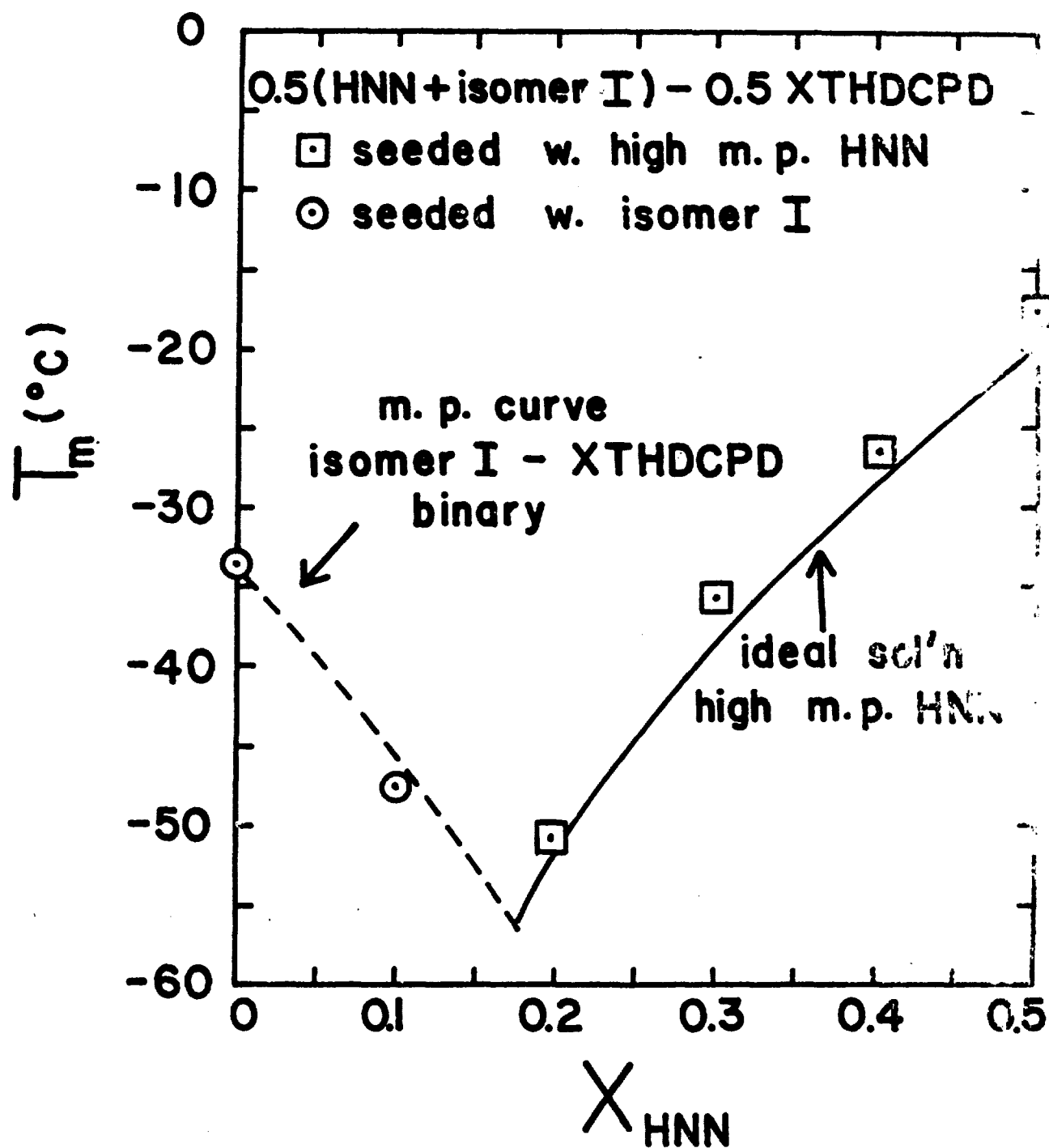


Fig. 8.

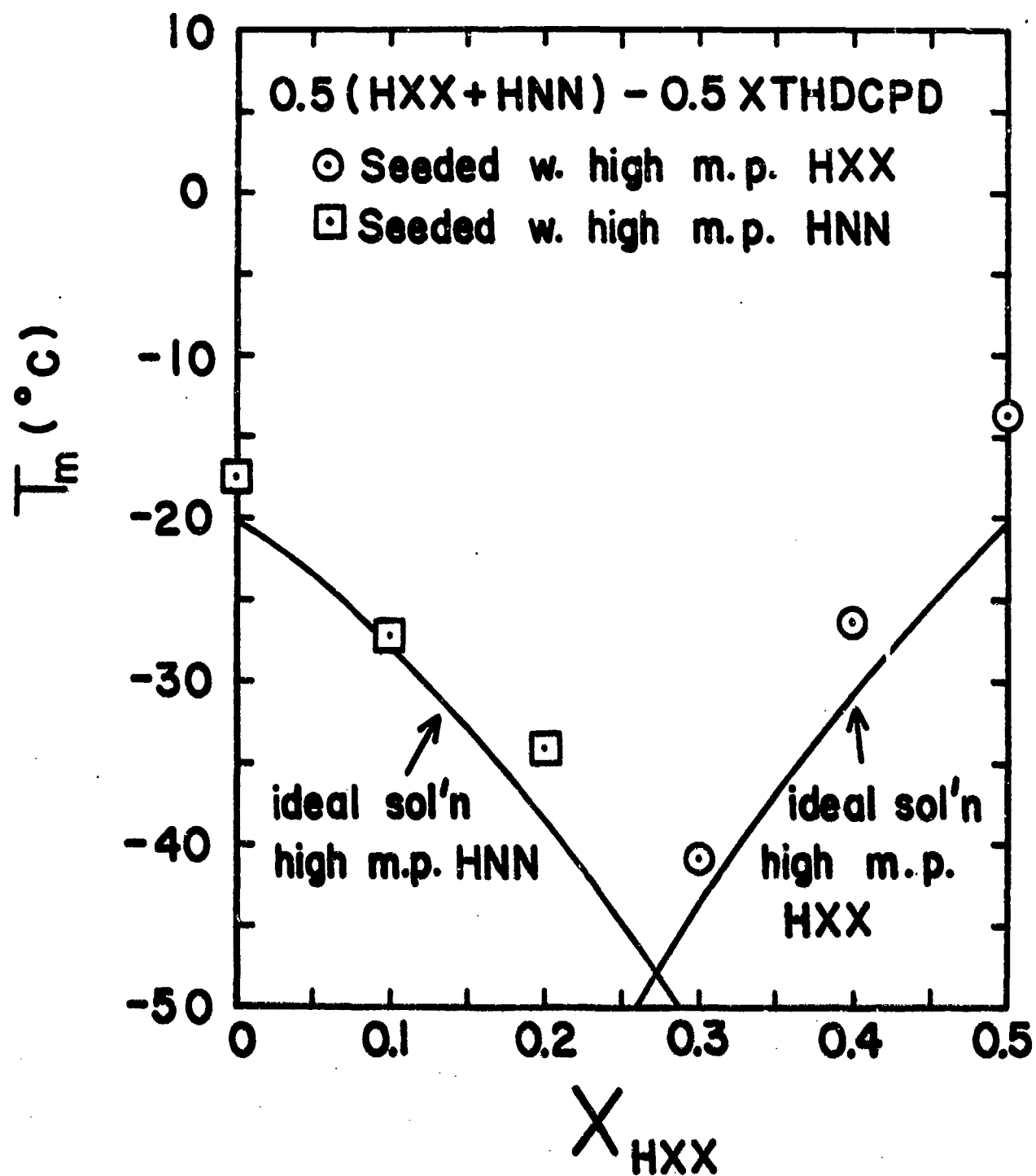


Fig. 9.

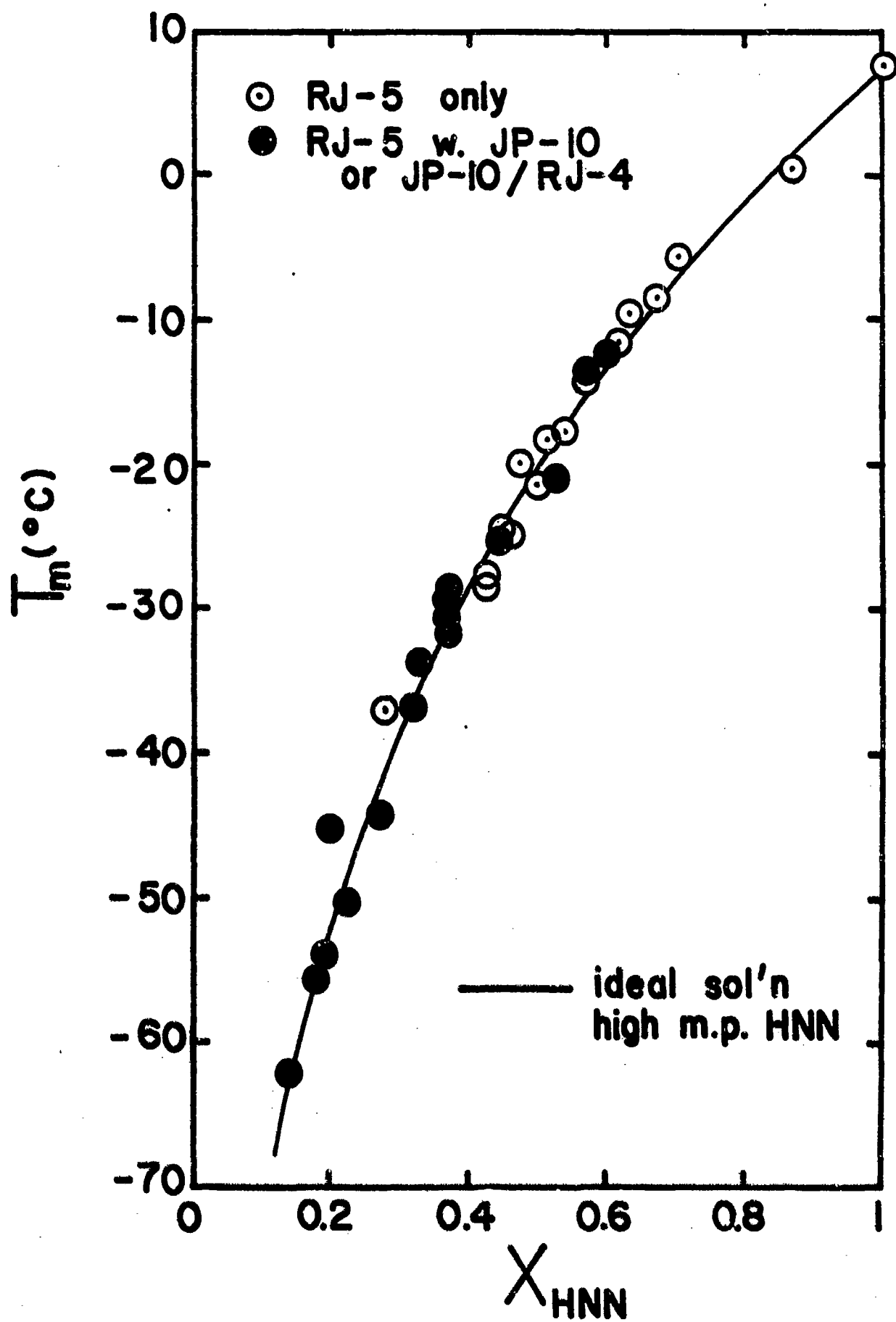


Fig. 10.

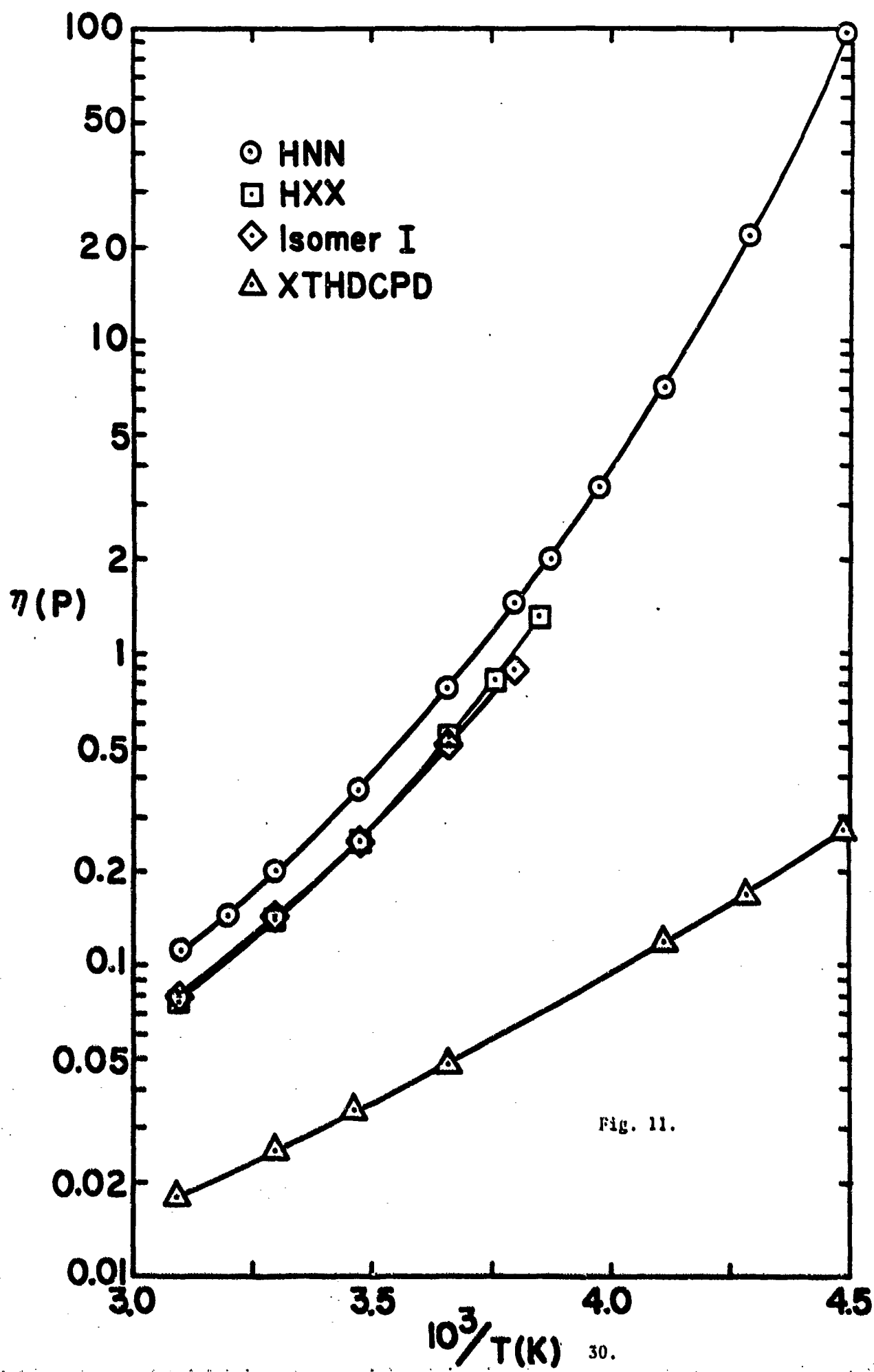


Fig. 11.

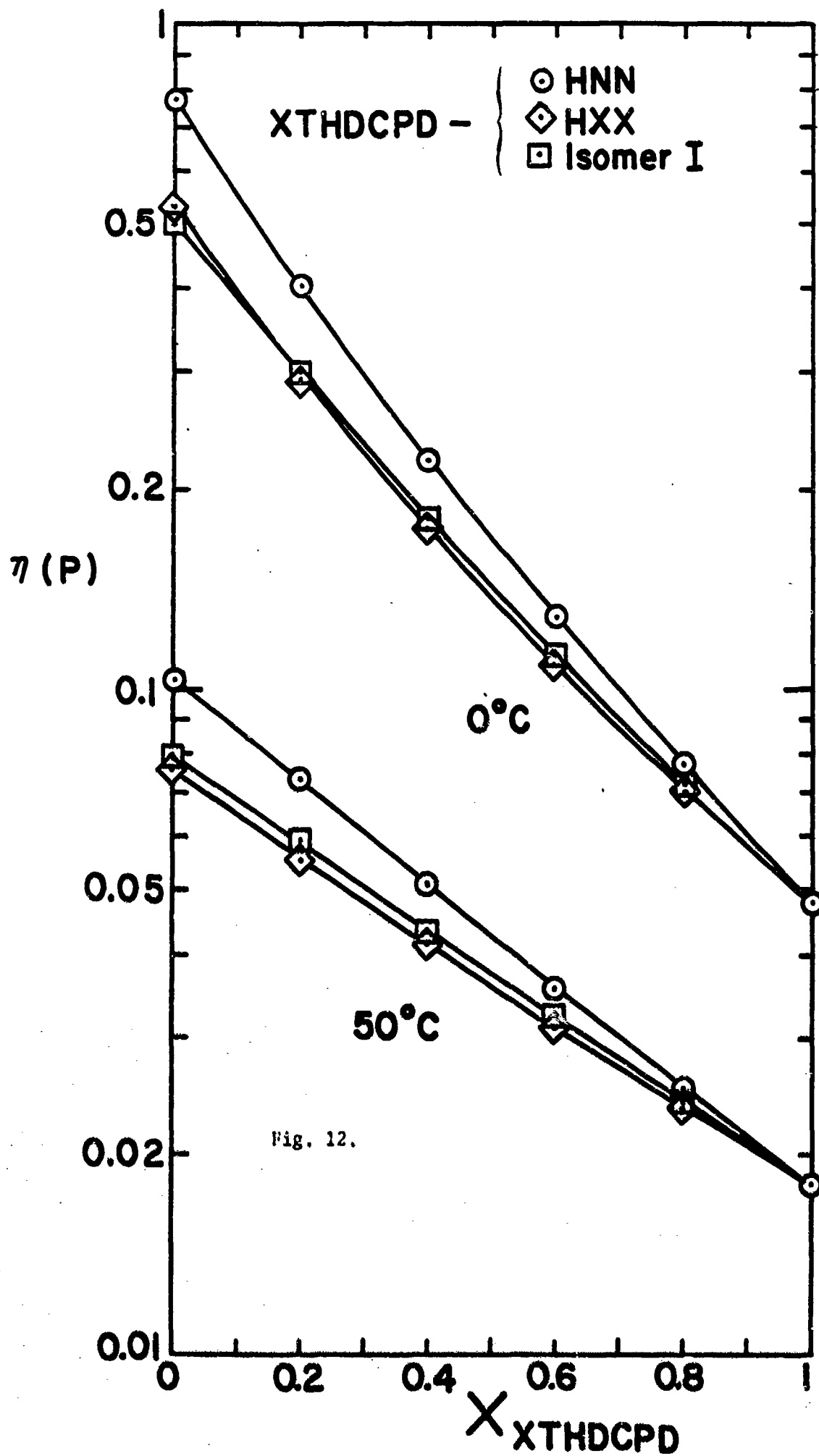


Fig. 12.

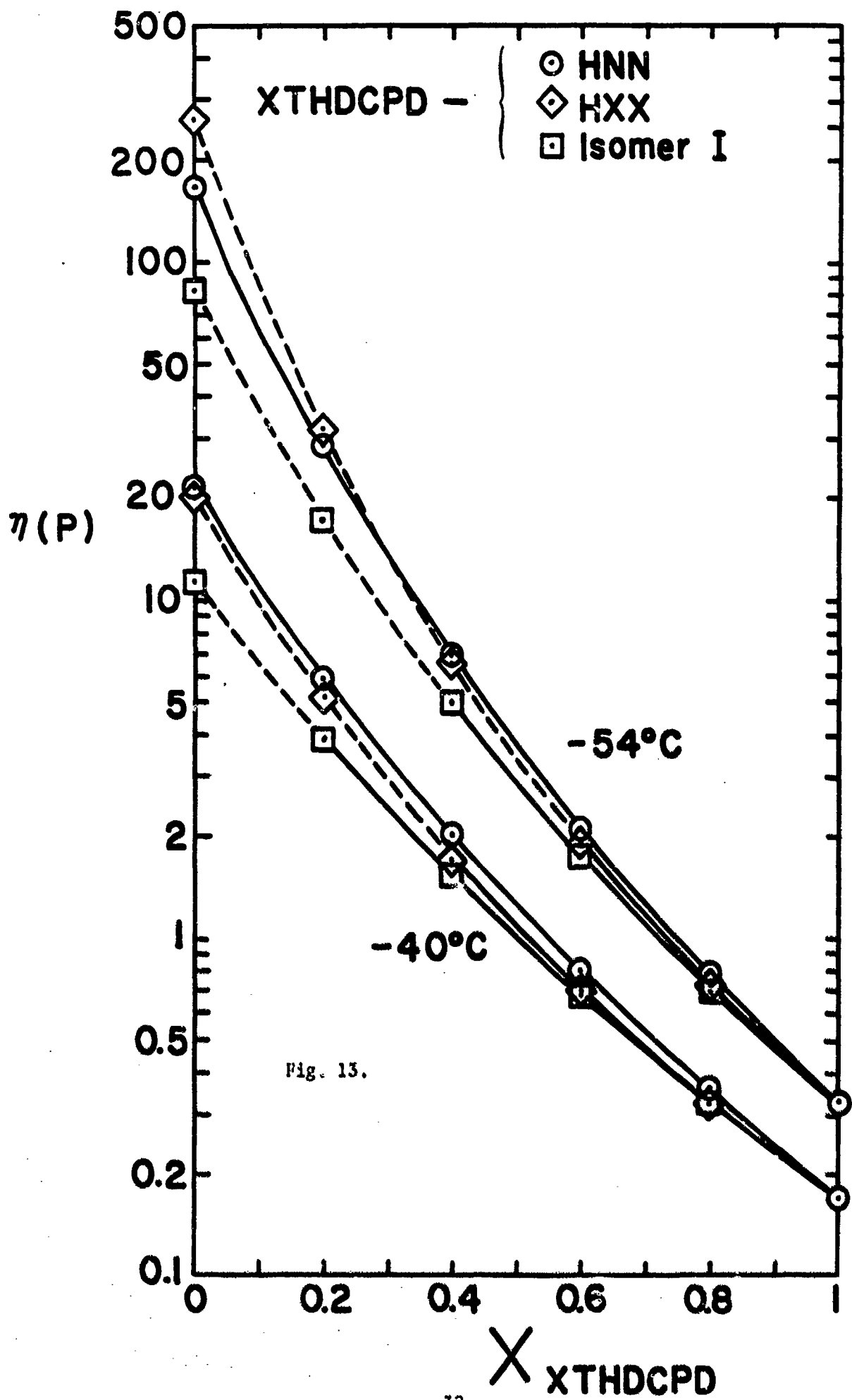


TABLE I. Melting point versus composition for blends of PHDNBD isomers HNN (99.9%), HXX (99.9%) and isomer I (97%) with themselves and with XTHDCPD (99.9%).

M.P.'S OF XTHDCPD-ISOMER I MIXTURES

COMP. (MOL%)		NO. DET'NS	M.P. (DEG C)	SEED CRYSTALS
ISO I	XTHDCPD			
100.0	0	4	15.3+-0.3	NONE
90.0	10.0	4	6.4+-0.3	NONE
90.0	10.0	4	6.4+-0.3	ISO I, HI M.P.
80.1	19.9	2	- 2.6+-0.3	NONE
80.1	19.9	3	- 2.6+-0.3	ISO I, HI M.P.
70.0	30.0	3	-13.1+-0.3	ISO I, HI M.P.
60.1	39.9	3	-22.5+-0.5	ISO I, HI M.P.
50.1	49.9	3	-33.6+-0.5	ISO I, HI M.P.
40.0	60.0	3	-44.5+-0.5	ISO I, HI M.P.
30.0	70.0	3	-59.9+-1.1	ISO I, HI M.P.

M.P.'S OF HNN-XTHDCPD MIXTURES

COMP. (MOL%)		NO. DET'NS	M.P. (DEG C)	SEED CRYSTALS
HNN	XTHDCPD			
100.0	0	9	7.5+-0.3	NONE
100.0	0	5	0.5+-0.3	NONE
94.7	5.3	7	- 2.3+-0.3	NONE
94.7	5.3	3	5.2+-0.3	HNN, HI M.P.
89.8	10.2	5	- 4.6+-0.3	NONE
89.8	10.2	3	2.6+-0.3	HNN, HI M.P.
79.7	20.3	3	- 9.9+-0.3	NONE
79.7	20.3	3	- 1.7+-0.3	HNN, HI M.P.
69.3	30.7	3	-13.6+-0.3	NONE
69.3	30.7	3	- 6.9+-0.3	HNN, HI M.P.
60.0	40.0	5	-11.8+-0.3	NONE
60.0	40.0	4	-19.6+-0.3	HNN, LO M.P.
54.6	45.4	3	-24.7+-0.3	NONE
54.6	45.4	2	-13.9+-0.4	HNN, HI M.P.
49.9	50.1	3	-17.9+-0.3	NONE
49.9	50.1	3	-27.4+-0.9	HNN, LO M.P.
44.6	55.4	6	-21.9+-0.3	HNN, HI M.P.
40.0	60.0	3	-25.1+-1.1	HNN, HI M.P.
35.2	64.8	3	-30.0+-0.6	HNN, HI M.P.
27.8	72.2	3	-37.5+-0.5	HNN, HI M.P.
25.2	74.8	3	-41.4+-0.5	HNN, HI M.P.
20.0	80.0	3	-47.6+-0.3	HNN, HI M.P.
15.0	85.0	2	-55.4+-0.9	HNN, HI M.P.
9.8	90.2	2	-59.6+-0.4	HNN, HI M.P.

M.P.'S OF HXX - XTHDCPD MIXTURES

COMP. (MOL%)		NO. DET'NS	M.P. (DEG C)	SEED CRYSTALS
HXX	XTHDCPD			
100.0	0	3	17.6+-0.3	NONE
100.0	0	3	11.3+-0.3	NONE
96.9	13.1	3	5.1+-0.3	NONE
96.9	13.1	3	19.0+-0.3	HXX, HI M.P.
74.6	25.4	3	- 1.3+-0.3	NONE
74.6	25.4	3	2.3+-0.5	HXX, HI M.P.
63.1	36.9	4	- 7.8+-0.3	NONE
63.1	36.9	3	- 5.2+-0.3	HXX, HI M.P.
63.1	36.9	1	- 7.8+-0.3	HXX, LO M.P.
52.3	47.7	3	-15.7+-0.3	NONE
52.3	47.7	3	-13.6+-0.3	HXX, HI M.P.
42.2	57.8	3	-23.4+-0.3	NONE
42.2	57.8	3	-21.2+-0.3	HXX, HI M.P.
32.8	67.2	3	-33.9+-0.8	HXX, LO M.P.
32.8	67.2	3	-31.9+-0.5	HXX, HI M.P.
28.3	71.1	2	-54.0+-1.1	NONE
28.3	71.1	2	-52.4+-1.1	HXX, HI M.P.

M.P.'S OF HNN - ISOMER I MIXTURES

COMP. (MOL%)		NO. DET'NS	M.P. (DEG C)	SEED CRYSTALS
ISOMER I	HNN			
100.0	0	3	15.3+-0.3	NONE
99.9	10.1	3	6.4+-0.3	ISO I, HI M.P.
79.9	20.1	3	- 1.3+-0.5	ISI I, HI M.P.
70.0	30.0	3	- 9.4+-0.5	ISO I, HI M.P.
59.7	40.3	3	-19.5+-0.8	ISO I, HI M.P.
59.7	40.3	1	-19.5+-0.3	HNN, HI M.P.
55.0	45.0	3	-25.8+-0.3	ISO I, HI M.P.
55.0	45.0	3	-22.5+-0.3	HNN, HI M.P.
50.0	50.0	2	-31.7+-0.3	ISO I, HI M.P.
50.0	50.0	3	-19.5+-0.5	HNN, HI M.P.
40.0	60.0	3	-12.6+-0.5	HNN, HI M.P.
30.3	69.7	3	- 6.2+-0.3	HNN, HI M.P.
20.0	80.0	3	- 1.3+-0.3	HNN, HI M.P.
10.0	90.0	3	9.6+-0.3	HNN, HI M.P.
0	100.0	9	7.5+-0.3	NONE

M.P.'S OF HXX-HNN MIXTURES

COMP. (MOL%)		NO. DET'NS	M.P. (DEG C)	SEED CRYSTALS
HXX	HNN			
100.0	0	3	17.3+-0.3	NONE
100.0	0	3	11.3+-0.3	NONE
97.0	3.0	3	9.0+-0.3	HXX, LO M.P.
97.0	3.0	3	15.7+-0.4	HXX, HI M.P.
95.0	5.0	3	- 0.5+-0.5	NONE
95.0	5.0	3	14.7+-0.3	HXX, HI M.P.
90.0	10.0	3	- 3.9+-0.5	NONE
90.0	10.0	3	11.0+-0.5	HXX, HI M.P.
84.4	15.6	3	- 4.2+-0.3	NONE
84.4	15.6	3	- 4.9+-0.3	NONE
84.4	15.6	3	7.4+-0.3	HXX, HI M.P.
75.0	25.0	3	- 7.8+-0.3	NONE
75.0	25.0	3	1.3+-0.5	HXX, HI M.P.
66.2	33.8	3	-11.3+-0.5	NONE
66.2	33.8	3	- 4.4+-0.3	HXX, HI M.P.
59.2	40.8	3	-16.1+-0.3	NONE
59.2	40.8	3	-12.3+-0.3	HXX, HI M.P.
55.0	45.0	3	-17.1+-0.5	NONE
55.0	45.0	3	-16.3+-0.5	HXX, HI M.P.
48.4	51.6	3	-21.7+-0.3	HNN, LO M.P.
48.4	51.6	3	-20.9+-0.8	HNN, HI M.P.
48.4	51.6	2	-22.3+-0.5	HXX, HI M.P.
48.4	51.6	2	-22.8+-0.5	HXX, HI M.P.
40.0	60.0	3	-28.3+-0.8	NONE
40.0	60.0	3	-14.7+-0.5	HNN, HI M.P.
40.0	60.0	2	-28.3+-0.3	HNN, LO M.P.
40.0	60.0	2	-14.7+-0.5	HNN, HI M.P.
30.0	70.0	3	-30.0+-0.8	NONE
30.0	70.0	3	- 7.8+-0.5	HNN, HI M.P.
20.0	80.0	3	-12.1+-0.3	NONE
20.0	80.0	3	- 1.8+-0.5	HNN, HI M.P.
10.0	90.0	3	- 3.9+-0.3	NONE
10.0	90.0	3	4.1+-0.5	HNN, HI M.P.
0	100.0	9	7.5+-0.3	NONE
0	100.0	5	0.5+-0.3	NONE

M.P.'S OF 0.5(HNN + ISOMER I) - 0.5 XTHDCPD MIXTURES

COMP. (MOL%)			NO. DET'NS	M.P. (DEG C)	SEED CRYSTALS
ISO I	HNN	XTHDCPD			
50.1	0	49.9	3	-33.6+-0.3	ISO I, HI M.P.
40.0	10.0	50.0	3	-47.7+-0.5	ISO I, HI M.P.
30.0	20.0	50.0	2	-50.9+-0.5	ISO I, HI M.P.
30.0	20.0	50.0	1	-50.9+-0.3	HNN, HI M.P.
19.9	30.1	50.0	3	-35.6+-0.5	HNN, HI M.P.
9.9	40.2	49.9	3	-26.4+-0.3	HNN, HI M.P.
0	50.0	50.0	3	-17.9+-0.3	NONE

M.P.'S OF 0.5(HNN + HXX) - 0.5 XTHDCPD MIXTURES

COMP. (MOL%)			NO. DET'NS	M.P. (DEG C)	SEED CRYSTALS
HXX	HNN	XTHDCPD			
50.0	0	50.0	3	-13.9+-0.3	HXX, HI M.P.
40.0	10.0	50.0	3	-26.4+-0.5	HXX, HI M.P.
30.0	20.0	50.0	3	-41.0+-0.5	HNN, HI M.P.
30.0	20.0	50.0	1	-41.0+-0.3	HXX, HI M.P.
20.0	30.0	50.0	3	-34.2+-0.5	HNN, HI M.P.
10.0	40.0	50.0	3	-27.2+-0.5	HNN, HI M.P.
0	50.0	50.0	3	-17.9+-0.3	NONE

TABLE II. Thermodynamic fusion data for HNN
and HXX PHDNBD isomers (molecular
weight 186.3 g/mol)

<u>Crystal</u>	<u>$T_{m,i}^{\circ}$ (K)</u>	<u>$\Delta \bar{H}_{f,i}$ (cal/mol)</u>	<u>$\Delta \bar{C}_{p,i}$ (cal/mol K)</u>
HNN, high m.p.	280.7 $\pm$ 0.3	3720 $\pm$ 50	11.6 $\pm$ 1.7
HNN, low m.p.	273.7 $\pm$ 0.3	2000 $\pm$ 70	-
HXX, high m.p.	290.2 $\pm$ 0.3	2850 $\pm$ 40	7.3 $\pm$ 0.7
HXX, low m.p.	284.5 $\pm$ 0.3	3150 $\pm$ 70	-

TABLE III. Heat capacities of crystal and liquid HNN and HXX PHDNBD isomers.

$$C_p(\text{cal/g } ^\circ\text{C}) = a + bT(^{\circ}\text{C})$$

<u>Material</u>	<u>T range ($^{\circ}\text{C}$)</u>	<u>a</u>	<u>b</u>	<u>Std. Dev.</u>
HNN (high m.p. cryst.)	-48 to -3	0.249	1.07×10^{-3}	0.005
HNN (liquid)	21 to 52	0.312	0.94×10^{-3}	0.004
HXX (high m.p. cryst.)	-37 to 8	0.265	1.46×10^{-3}	0.002
HXX (liquid)	16 to 61	0.312	1.03×10^{-3}	0.002

TABLE IV. Densities and shear viscosities
as a function of temperature for
PHDNBD isomers HNN (99.9%),
HXX (99.9%) and isomer I (97%)
and their blends with XTHDCPD
(99.9%).

HNN

TEMP. (DEG C)	DENSITY (G/CM ³)	VISCOSITY (POISE)
-50.75	1.144	96.7
-40.13	1.136	21.74
-29.94	1.127	7.03
-21.79	1.122	3.387
-15.19	1.117	2.023
-10.23	1.113	1.446
+ 0.04	1.105	0.768
+14.90	1.094	0.3663
+29.76	1.083	0.2010
+39.62	1.076	0.1436
+49.41	1.069	0.1057

80 MOL% HNN & 20 MOL% XTHDCPD

TEMP. (DEG C)	DENSITY (G/CM ³)	VISCOSITY (POISE)
-55.20	1.121	33.46
-50.64	1.117	18.32
-30.22	1.102	2.531
-14.90	1.090	0.886
- 0.04	1.079	0.403
+15.24	1.066	0.2115
+29.82	1.055	0.1276
+49.86	1.041	0.0728

60 MOL% HNN & 40 MOL% XTHDCPD

TEMP. (DEG C)	DENSITY (G/CM ³)	VISCOSITY (POISE)
-54.28	1.093	7.07
-50.77	1.089	5.01
-40.19	1.081	2.010
-14.81	1.062	0.427
- 0.04	1.051	0.2223
+15.06	1.040	0.1285
+30.01	1.028	0.0827
+49.71	1.013	0.0507

40 MOL% HNN & 60 MOL% XTHDCPD

TEMP. (DEG C)	DENSITY (G/CM ³)	VISCOSITY (POISE)
-54.01	1.061	2.106
-50.74	1.058	1.641
-41.60	1.052	0.874
-30.21	1.043	0.456
-13.08	1.031	0.2253
- 0.02	1.020	0.1282
+14.58	1.009	0.0820
+29.95	0.996	0.0545
+49.78	0.982	0.03525

20 MOL% HNN & 80 MOL% XTHDCPD

TEMP. (DEG C)	DENSITY (G/CM ³)	VISCOSITY (POISE)
-50.25	1.025	0.612
-40.28	1.017	0.3555
-30.15	1.010	0.2230
-15.07	0.998	0.1245
0.00	0.987	0.0778
+14.84	0.976	0.0520
+30.07	0.964	0.03662
+49.86	0.949	0.02490

HXX

TEMP. (DEG C)	DENSITY (G/CM ³)	VISCOSITY (POISE)
-13.85	1.109	1.312
- 7.12	1.103	0.818
- 0.23	1.090	0.536
+15.07	1.086	0.2480
+29.83	1.075	0.1393
+49.86	1.061	0.0756

80 MOL% HXX & 20 MOL% XTHDCPD

TEMP. (DEG C)	DENSITY (G/CM ³)	VISCOSITY (POISE)
-25.00	1.085	1.315
-15.32	1.078	0.675
- 0.19	1.066	0.2953
+14.84	1.055	0.1568
+29.85	1.044	0.0946
+49.86	1.029	0.0552

60 MOL% HXX & 40 MOL% XTHDCPD

TEMP. (DEG C)	DENSITY (G/CM ³)	VISCOSITY (POISE)
-47.61	1.077	3.311
-40.37	1.071	1.743
-30.47	1.064	0.833
-15.18	1.052	0.3428
+ 0.08	1.041	0.1735
+14.95	1.029	0.1021
+29.86	1.018	0.0662
+49.95	1.003	0.0411

40 MOL% HXX & 60 MOL% XTHDCPD

TEMP. (DEG C)	DENSITY (G/CM ³)	VISCOSITY (POISE)
-55.25	1.056	2.116
-50.30	1.052	1.411
-40.40	1.044	0.704
-30.23	1.035	0.3887
-15.05	1.024	0.1906
- 0.28	1.013	0.1099
+14.87	1.002	0.0691
+29.87	0.991	0.0472
+49.92	0.976	0.03090

20 MOL% HXX & 80 MOL% XTHDCPD

TEMP. (DEG C)	DENSITY (G/CM ³)	VISCOSITY (POISE)
-55.42	1.026	0.783
-50.34	1.022	0.570
-40.29	1.014	0.3262
-29.99	1.006	0.2019
-14.86	0.995	0.1126
- 0.08	0.984	0.0708
+14.75	0.973	0.0479
+29.83	0.961	0.03413
+49.81	0.946	0.02333

ISOMER I

TEMP. (DEG C)	DENSITY (G/CM ³)	VISCOSITY (POISE)
-10.16	1.105	0.839
- 0.18	1.097	0.506
+14.86	1.086	0.2487
+29.89	1.073	0.1420
+49.85	1.058	0.0785

80 MOL% ISOMER I & 20 MOL% XTHDCPD

TEMP. (DEG C)	DENSITY (G/CM ³)	VISCOSITY (POISE)
-38.99	1.102	3.485
-30.74	1.097	1.768
-15.20	1.085	0.638
+ 0.05	1.073	0.2973
+15.04	1.062	0.1626
+29.89	1.048	0.0999
+49.85	1.033	0.0586

60 MOL% ISOMER I & 40 MOL% XTHDCPD

TEMP. (DEG C)	DENSITY (G/CM ³)	VISCOSITY (POISE)
-50.05	1.084	3.405
-40.37	1.077	1.553
-30.11	1.067	0.777
-15.37	1.056	0.3498
- 0.24	1.044	0.1829
+15.01	1.034	0.1075
+29.90	1.022	0.0698
+49.86	1.006	0.0432

40 MOL% ISOMER I & 60 MOL% XTHDCPD

TEMP. (DEG C)	DENSITY (G/CM ³)	VISCOSITY (POISE)
-54.55	1.058	1.813
-50.24	1.054	1.311
-40.59	1.047	0.693
-30.28	1.039	0.3919
-15.01	1.027	0.1965
- 0.19	1.016	0.1144
+15.02	1.004	0.0719
+29.72	0.993	0.0495
+49.84	0.978	0.03212

20 MOL% ISOMER I & 80 MOL% XTHDCPD

TEMP. (DEG C)	DENSITY (G/CM ³)	VISCOSITY (POISE)
-55.18	1.027	0.745
-50.28	1.023	0.555
-40.29	1.016	0.3248
-30.13	1.006	0.2051
-15.16	0.995	0.1149
- 0.17	0.984	0.0720
+15.06	0.973	0.0483
+29.78	0.962	0.03472
+49.86	0.946	0.02361

XTHDCPD (RUN I)

<u>TEMP.</u> <u>(DEG C)</u>	<u>DENSITY</u> <u>(G/CM³)</u>	<u>VISCOSITY</u> <u>(POISE)</u>
-54.47	0.991	0.3320
-50.45	0.989	0.2713
-39.80	0.981	0.1698
-30.22	0.974	0.1171
0.00	0.951	0.0481
+15.34	0.939	0.03369
+29.97	0.927	0.02488
+49.85	0.913	0.01765

XTHDCPD (RUN II)

<u>TEMP.</u> <u>(DEG C)</u>	<u>DENSITY</u> <u>(G/CM³)</u>	<u>VISCOSITY</u> <u>(POISE)</u>
-55.00	0.993	0.3361
-50.37	0.988	0.2683
-40.30	0.982	0.1718
-30.07	0.973	0.1160
-15.18	0.962	0.0715
- 0.01	0.951	0.0475
+14.85	0.939	0.03366
+29.86	0.928	0.02496
+49.86	0.913	0.01773

TABLE V.

PARAMETERS FOR DENSITY EQUATIONS FOR HNN, HXX, ISOMER I, XTHDCPD
AND THEIR MIXTURES WITH XTHDCPD

$$D(\text{G/CM}^3) = D(0) - B \cdot T(\text{DEG C})$$

COMPOSITION (MOLE FRACTION)	T RANGE (DEG C)	D(0)	B*10 ¹⁴	STD. DEV. OF D
HNN	-50 TO 50	1.105	7.49	0.0004
HXX	-14 TO 50	1.098	7.50	0.0004
ISOMER I	-10 TO 50	1.097	7.81	0.0002
XTHDCPD RUN I	-54 TO 50	0.951	7.60	0.0003
XTHDCPD RUN II	-55 TO 50	0.951	7.60	0.0004
.2 HNN-.8 XTHDCPD	-52 TO 50	0.987	7.59	0.0001
.4 HNN-.6 XTHDCPD	-54 TO 50	1.020	7.64	0.0003
.6 HNN-.4 XTHDCPD	-54 TO 50	1.051	7.56	0.0003
.8 HNN-.2 XTHDCPD	-55 TO 50	1.079	7.61	0.0005
.2 HXX-.8 XTHDCPD	-55 TO 50	0.984	7.60	0.0003
.4 HXX-.6 XTHDCPD	-55 TO 50	1.013	7.59	0.0006
.6 HXX-.4 XTHDCPD	-48 TO 50	1.041	7.59	0.0002
.8 HXX-.2 XTHDCPD	-25 TO 50	1.066	7.49	0.0001
.2 I -.8 XTHDCPD	-55 TO 50	0.984	7.63	0.0005
.4 I -.6 XTHDCPD	-55 TO 50	1.016	7.67	0.0003
.6 I -.4 XTHDCPD	-50 TO 50	1.045	7.69	0.0006
.8 I -.2 XTHDCPD	-39 TO 50	1.072	7.84	0.0005

TABLE VI.

BEST FIT VTF EQUATION PARAMETERS FOR SHEAR VISCOSITY OF HNN, HXX, ISOMER I, XTHDCPD AND THEIR MIXTURES WITH XTHDCPD

$$\text{LN VISC}(P) = A + B/[T(K) - T_0]$$

COMPOSITION (MOLE FRACTION)	T RANGE (DEG C)	A	B (DEG K)	T ₀ (DEG K)	STD.DEV. LN(VISC)
HNN	-50 TO 50	-7.168	850.75	150	0.0043
HXX	-14 TO 50	-6.765	656.87	166	0.0006
ISOMER I	-10 TO 50	-7.041	768.95	152	0.0025
XTHDCPD RUN I	-54 TO 50	-7.752	881.78	86	0.0060
XTHDCPD RUN II	-55 TO 50	-7.653	847.96	89	0.0016
.2 HNN-.8 XTHDCPD	-50 TO 50	-7.611	874.68	100	0.0044
.4 HNN-.6 XTHDCPD	-54 TO 50	-7.401	840.44	116	0.0036
.6 HNN-.4 XTHDCPD	-54 TO 50	-7.244	827.14	129	0.0044
.8 HNN-.2 XTHDCPD	-55 TO 50	-7.226	847.54	139	0.0044
.2 HXX-.8 XTHDCPD	-55 TO 50	-7.380	776.05	109	0.0030
.4 HXX-.6 XTHDCPD	-55 TO 50	-7.164	727.65	126	0.0020
.6 HXX-.4 XTHDCPD	-48 TO 50	-6.992	692.87	141	0.0021
.8 HXX-.2 XTHDCPD	-25 TO 50	-6.893	674.21	154	0.0013
.2 I -.8 XTHDCPD	-55 TO 50	-7.518	830.82	103	0.0023
.4 I -.6 XTHDCPD	-55 TO 50	-7.394	819.90	116	0.0027
.6 I -.4 XTHDCPD	-50 TO 50	-7.293	810.50	128	0.0022
.8 I -.2 XTHDCPD	-39 TO 50	-7.165	792.64	140	0.0019