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Measurements of the following physical properties have been carried out for four isomers of hydrogenated norbornadiene dimers and for exo-tetrahydrodicyclopentadiene: enthalpies of fusion and solid and liquid heat capacities of the pure compounds; melting points, liquid densities and shear viscosities of the pure compounds and mixtures. The mixtures exhibit no solid solution or compound formation on freezing, but their freezing points can be predicted only approximately

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20. on the assumption of ideal solution behavior. Molar volumes of mixtures are additive with respect to the liquid molar volumes. Empirical equations have been developed which are capable of predicting accurately the mixture viscosities over the entire composition and temperature range studied.

PHYSICAL PROPERTIES OF HYDROGENATED DIMERS OF NORBORNADIENE AND EXO-TETRAHYDRODICYCLOPENTADIENE AND THEIR MIXTURES*

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SUMMARY

Measurements of the following physical properties have been carried out for four isomers of hydrogenated norbornadiene dimers and for exo-tetrahydrodicyclopentadiene: enthalpies of fusion and solid and liquid heat capacities of the pure compounds; melting points, liquid densities and shear viscosities of the pure compounds and mixtures. The mixtures exhibit no solid solution or compound formation on freezing, but their freezing points can be predicted only approximately on the assumption of ideal solution behavior. Molar volumes of mixtures are additive with respect to the liquid molar volumes. Empirical equations have been developed which are capable of predicting accurately the mixture viscosities over the entire composition and temperature range studied.

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I. INTRODUCTION

The principal drawback to using RJ-5 fuels, which contain hydrogenated dimers of norbornadiene (NBD), as high energy density missile fuels are the high freezing points and viscosities exhibited by these compounds and their mixtures. In an effort to understand and hence to control these properties over the past two years we have carried out a basic research program aimed at characterizing fundamental physical properties (enthalpy of fusion, heat capacity, density, and shear viscosity) of the components of these mixtures and using them to predict freezing and viscous flow behavior of the corresponding fuel blends. In the present paper we summarize the results of our efforts to date.

II. EXPERIMENTAL SECTION

Studies were carried out on samples of four hydrogenated dimers of NBD and of one lower molecular weight fuel diluent (exo-tetrahydrodicyclopendadiene). The structures of these compounds are shown in Fig. 1, along with the abbreviations (HXX, XTHDCPD, etc.) by which they will be referred to in the remainder of the paper. Their formulae and molecular weights M are given in Table I. The samples were obtained from Dr. A. Schneider of Suntech, Inc. Their purities, as determined by him using vapor phase chromatography (VPC), are also given in Table I. In all cases the impurities were other isomers of the compound. All mixtures studied were prepared by weight from these samples.

Enthalpies of fusion, ΔH_f, and crystal and liquid heat capacities, c_p, were determined for the five compounds using a Perkin-Elmer Model DSC-2 differential scanning calorimeter (DSC).

Densities ρ (accuracy ~ 0.3%) were measured by means of a dilatometer and shear viscosities η (accuracy ~ 1% above 0°C, ~ 2% below 0°C) by means of factory-calibrated Ubbelohde semi-micro capillary viscometers from the Cannon Instrument Co. All of these determinations are described in greater detail in previous reports[1-3].

III. THERMAL DATA AND FREEZING OF MIXTURES

A. Enthalpies of Fusion, Melting Points, and Heat Capacities

In Fig. 2 is shown a typical plot of heat capacity versus temperature measured by DSC while heating a sample of HXX. The area under the peak in the c_p vs. T plot corresponds to the enthalpy increase during melting, while the linear regions above and below the fusion peak are respectively the liquid and crystal heat capacities.

Because the samples used in our study were not completely pure, they melted over a range in temperature, rather than sharply at a single temperature. As explained previously[1,3], this means that the enthalpy of fusion and equilibrium melting point of the pure compound , T_o, cannot be determined directly from the area and position of the fusion peak in c_p vs. T plot. Rather a detailed analysis[1,3] incorporating a semi-empirical correction method must be employed to extract ΔH_f and T_o from the data; the analysis yields in addition the mole fraction of impurity in the sample. In Table I are listed the enthalpies of fusion, pure compound melting points and impurity mole percents obtained from analysis of our DSC results[3].

The crystal and liquid heat capacities of a given compound were linear functions of temperature and within experimental error the slope of the c_p vs. T plot was the same for liquid and crystal. Heat capacity results for the five compounds are given in Table II in terms of least squares fits of the experimental results to equations of the form

$$c_p(\text{cal/gK}) = c_p(T_o) + b[T(K) - T_o]$$

where $c_p(T_o)$ is the heat capacity at the pure compound melting point T_o. The slope b for each compound was constrained in the fitting procedure to be the same for the crystal as for the liquid. No c_p results are reported for XTHDCPD crystal because of the difficulty in obtaining good DSC data at the very low temperatures below the XTHDCPD melting point.

The four NBD hydrogenated dimers exhibit an unusually wide range in their respective ΔH_f values. It sometimes happens that a crystal will exhibit an unusually low ΔH_f and high T_o compared to similar compounds due to the occurrence of crystal-crystal phase transitions below the melting point. No such transitions above 200K were observed by DSC, however, for the NBD hydrogenated dimers.

In Table III the crystal and liquid heat capacities of the five compounds are compared at common temperatures. It appears that at a given temperature the respective crystal and liquid heat capacities are all virtually the same.

B. Predicition of Mixture-Melting Points

Provided that there is no formation of solid solutions or solid compounds on freezing, addition of other components to a pure liquid i will lower its equilibrium freezing point T_i. The dependence of T_i on the mole fraction of component i in the solution is given by the expression[4]

$$\ln X_i = \frac{\Delta H_{fi}}{R} \left(\frac{1}{T_{oi}} - \frac{1}{T_i}\right) - \frac{\Delta Cp_{fi}}{R} \left(1 - \frac{T_{oi}}{T_i} + \ln \frac{T_{oi}}{T_i}\right) - \ln \gamma_i \qquad (1)$$

where X_i = mole fraction of component i in solution

T_{oi} = equilibrium freezing point of pure component i in absolute degrees (K)

T_i = equilibrium freezing point of component i in solution in absolute degrees (K)

ΔH_{fi} = molar enthalpy of fusion of pure i at temperature T_{oi} (cal/mol)

ΔCp_{fi} = molar heat capacity difference between liquid and crystalline pure i at temperature T_{oi} (cal/mol K)

R = ideal gas constant = 1.987 cal/mol K

γ_i = activity coefficient of component i in solution

Each component i of the solution will have an equilibrium freezing point T_i at which the solid phase of i becomes stable with respect to the liquid phase of a given composition. The highest of these T_i is considered to be the equilibrium freezing point of the solution, i.e., the highest temperature at which a solid phase can exist in equilibrium with the liquid.

We have calculated freezing points T_i as a function of mole fraction X_i for each of the five compounds studied here using Eq. (1), the data in Tables I and II and assuming ideal solution behavior ($\gamma_i = 1$). For these calculations a value of 12 cal/mol K, estimated from the DSC fusion curve, was used for ΔC_{pf} for XTHDCPD. The results of these calculations are shown in Fig. 3 as plots of T_i (in K and °F) versus X_i for each of the compounds. Figure 3 may be used to estimate freezing points of fuel blends containing these compounds, as illustrated in the following example.

EXAMPLE Estimate the equilibrium freezing point of a blend of composition 36 wt % HNN, 24 wt % HXX and 40 wt % HTHDCPD.

It is first necessary to convert the compositions of each component i from wt % i to mole fraction X_i. This may be done using the expression

$$X_i = \frac{(\text{wt \% } i/M_i)}{\sum_k (\text{wt \% } k/M_k)} \qquad (2)$$

where M_i is the molecular weight of component i (cf. Table I) and the sum in the denominator is taken over all components k of the solution. The equilibrium freezing points T_i of each component are then read off Fig. 3. The values of X_i and the corresponding T_i are listed below.

component i	HNN	HXX	XTHDCPD
wt % i	36	24	40
X_i	0.31	0.21	0.48
T_i(°F)	-12	-52	-213

The highest of the T_i is the equilibrium freezing point of the solution. In this case the HNN isomer is predicted to freeze out at -12°F at equilibrium.

Additional examples and comments on the use of Fig. 3 are given in a previous report[5]. In particular, it should be noted that the T_i values calculated here are equilibrium freezing points. In reality these fuel blends tend to exhibit extensive supercooling, and the various components will generally be observed to freeze only on long standing at temperatures well below the T_i value. Once frozen, however, the various components will not melt completely until heated to their equilibrium freezing points T_i. Hence the proper way to determine the equilibrium freezing point is to freeze the sample, heat it slowly and measure the temperature at which the last crystals just melt.

In Table IV comparison is made between some observed melting points (m.p.) of mixtures and those (i.e., the T_i values) calculated on the basis of ideal solution behavior via Fig. 3. The first four entries in Table IV are for the high purity specimens obtained from Sun Tech., Inc. In these cases the composition assigned is based on the mole fraction of impurity determined by DSC (Table I). The m.p.'s reported for the first four entries in the "DSC" column are those extracted from our analysis of the DSC fusion peaks[1,3]; note that these impure sample melting points are not the same as the pure compound melting points of Table I. For the next three entries in Table IV the m.p.'s reported in the "DSC" column correspond to the temperatures of the endothermic fusion peaks obtained during reheating on the DSC of mixtures which had been previously frozen on the DSC by cooling to low temperatures[1]. The m.p.'s in the "visual" column were obtained by allowing a frozen sample contained in a test tube or a viscometer to warm slowly in the thermostat bath and noting the temperature at which the last crystals melted. The second column in Table IV gives the mixture component i calculated to have the highest T_i for that composition. Differences between the experimental and calculated ideal solution melting points are given in the last column.

In general there is some disagreement between the experimental and calculated melting points of the mixtures. Part of this is due to the fact that the components used in making up the mixtures were not pure, but errors in composition due to this factor should in general contribute errors of less than 1°C to the calculated melting points. The compositions of mixtures melted on the DSC lie close to the calculated eutectic compositions; these were found to melt sharply over a narrow temperature range, as expected for a eutectic composition[1]. As the mole fraction of the highest melting component decreased so did the melting point, i.e., there appear to be no compositions with relative m.p. maxima, as would be observed if solid compounds formed on freezing. In most cases the observed m.p. is lower than the calculated value, indicating in these instances that no solid solutions are formed on freezing, which would tend to make the observed m.p. higher than the calculated value. These observations suggest that the disagreement between the observed and calculated m.p.'s is due to deviations of the liquid mixtures from ideality, i.e., the activity coefficient γ_i in Eq. (1) is not unity.

Large deviations from ideality are not required to account for the differences between the calculated and observed m.p.'s in Table IV. For example, for the 0.500 HXX - 0.500 HNN mixture the -9 °C m.p. discrepancy corresponds via Eq. (1) to an HNN activity coefficient, γ_{HNN}, of about 0.7. Using the regular solution theory expression[4]

$$RT \ln \gamma_{HNN} = w\ (1 - X_{HNN})^2$$

we get an interaction energy parameter w of about -700 cal/mol, which is not too large. Although small deviations from ideality affect m.p.'s of mixtures to a moderate degree, they have a much smaller effect on the calculation of compositions of minimum freezing point, i.e., the eutectics. Hence Fig. 3 may be used to determine fairly reliable minimum freezing point compositions.

IV. DENSITIES

The liquid densities ρ of all the pure compounds and their mixtures were found to vary linearly with temperature. Density results are given in Table V in the form of parameters obtained from least squares fits of the experimental data to the equation

$$\rho(\mathrm{g/cm^3}) = \rho(0) - b'\ T(^\circ\mathrm{C})$$

The scatter of the experimental points about the least squares lines is typically 0.1 to 0.2%. All of the mixtures appear to exhibit about the same density temperature coefficient, $d\rho/dT = -b' \simeq -8 \times 10^{-4}$ g/cm^3 °C. In Table VI we have compared the densities determined in the present work with those measured at a number of laboratories engaged in the investigation of RJ-5 type fuels for the compound XTHDCPD. This compound was chosen for comparison because most investigators have worked with fairly pure samples of it, so that the comparison is unlikely to be invalidated by composition discrepancies between different samples. Above -6.7°C the density results from the different laboratories agree within our experimental error of 0.3%, but at lower temperatures the discrepancies are somewhat larger.

In Fig. 4 are shown plots of molar volume $\bar{V}$ ($= \Sigma_i M_i X_i/\rho$) at 0°C as a function of composition for three of the binary mixtures studied by us. The plots are linear within experimental error, showing that for mixtures of NBD hydrogenated dimers and XTHDCPD the molar volumes are additive.

V. SHEAR VISCOSITIES

A. VTF Equation Fits

In Fig. 5 are shown two typical examples of the temperature dependence of the shear viscosity in form of Arrhenius plots of log η versus $10^3/T(K)$. The plots are curved, but may be described well by the semi-empirical Vogel-Tammann-Fulcher (VTF) equation[2,4].

$$\ln \eta \ (P) = A + B/[T(K) - T_2] \qquad (3)$$

where A,B, and T_2 are constants. The η vs. T data for all liquids studied were fit to Eq. (3) in the following fashion. A value of T_2 was chosen, the corresponding parameters A and B evaluated by a linear least squares fit of ln η vs. $1/(T_2 - T)$ and the standard deviation, Std. Dev. ln η, of the experimental data from the least squares line calculated. The value of T_2 was changed and

and the fit repeated until the value of T_2 (to the nearest 1K) corresponding to the minimum in Std. Dev. ln η was located. Typical sets of A,B, T_2 and Std. Dev. ln η obtained from fits to the pure HNN viscosity data are shown in Table VII. The best fit parameters (for $T_2 = 148$) are those in the second line, but parameters corresponding to T_2 values in the neighborhood of 148K also give a good description of the temperature dependence of the HNN viscosity.

In Table VIII the best fit parameters for Eq. (3) are listed for the liquids whose viscosity was studied. Std. Dev. ln η is typically about 0.01. Since $\Delta \ln \eta = \Delta\eta/\eta$, this means that the scatter of the data from the best fit curves is typically about 1%, so that the parameters of Table VIII may be used to calculate with good precision the viscosities of the respective liquids over the temperature ranges indicated. The solid lines in Fig. 5 have been calculated from the VTF equation parameters of Table VIII for HNN and XTHDCPD.

In Table IX shear viscosities for XTHDCPD of a number of different investigators are compared with those of the present study. At a given temperature the viscosities measured in different laboratories vary by as much as 20 to 30%, well outside of experimental error in most cases.

B. Master Viscosity Equation for Mixtures of NBD Hydrogenated Dimers

All of the mixtures containing only NBD hydrogenated dimers (the first 8 entries in Table VIII) exhibit about the same value of the best fit T_2 parameter, the mean T_2 value being 152 ± 4K. T_2 has been interpreted theoretically as the temperature at which the free volume[10] or configurational entropy[11] vanishes. For normal alkanes T_2 has been found to be a monotonically increasing function of molecular weight[12]. Hence it is not surprising that a group of highly similar hydrocarbons such as the NBD hydrogenated dimers should all exhibit approximately the same T_2 value. A good fit to the viscosities of all eight of the NBD hydrogenated dimer liquids studied can be obtained using the same T_2 value of 152K; Std. Dev. ln η in the worst case is 0.018.

Of equal interest is the fact that all of the NBD hydrogenated dimer liquids show approximately the same B value; the mean B for the first eight entries in Table VIII is 822 ± 58. The agreement between the B values is even better when they are compared for a constant T_2 value of 152K; in this case the mean B is 825 ± 17.

That all of the NBD hydrogenated dimers can be described to a good approximation by the same T_2 and B values means that the viscosities of all these liquids exhibit virtually identical temperature dependences on a logarithmic viscosity scale. This suggested a master viscosity equation capable of describing both the temperature and composition dependence of mixtures of NBS hydrogenated dimers:

$$\ln \eta \ (P) = \sum_i A_i X_i + \frac{B}{T(K) - T_2} \qquad (4)$$

with constant T_2 and B values. X_i is the mole fraction of component i, and the sum is taken over all the components if of the mixture. A fit to Eq. (4) of the combined viscosity data from all eight liquids containing only NBD hydrogenated dimers gave the following parameters

$$T_2 = 148 \tag{5a}$$

$$B = 872.7 \tag{5b}$$

$$A_{HXX} = -7.587 \tag{5c}$$

$$A_{HXN} = -7.319 \tag{5d}$$

$$A_{HNN} = -7.242 \tag{5e}$$

$$A_{PXtX} = -7.567 \tag{5f}$$

$$\text{Std. Dev. } \ln \eta = 0.020 \tag{5g}$$

According to Eq. (4) a plot of log $(\eta/\exp \sum_i A_i X_i)$ vs. $10^3/(T-T_2)$ should put the viscosities of all mixtures of NBD hydrogenated dimers on the same straight line. Such a plot is shown in Fig. 6; the solid line is calculated from Eq. (4) using the parameters of Eqs. (5). The small scatter about the line reflects the good precision with which Eq. (4) describes the data.

The engineering implications of the above should be obvious. Knowing only the composition of a mixture of the four NBD hydrogenated dimers studied here one can predict its viscosity at a temperature of interest using Eq. (4) and the parameters of Eq. (5). As an example in Table X we compare the experimental and calculated viscosities of a commercially produced RJ-5 fuel blend with composition (by VPC analysis) 0.2 HXN - 0.7 HNN - 0.1 PXtX. The agreement between the experimental and calculated viscosities is excellent.

It should also be noted that Eqs. (4) and (5) predict that at constant temperature the viscosity of mixtures of NBD hydrogenated dimers varies in monotonic fashion with composition. There are no mixtures which exhibit viscosity minima with respect to the pure components. In fact the four NBD hydrogenated dimers studied here all exhibit rather similar viscosities. From Eqs. (4) and (5) one predicts that at -40°C the composition of minimum viscosity should be pure supercooled HXX (14.2) and that of maximum viscosity pure supercooled HNN (20.1 P).

C. Master Viscosity Equation for Mixtures of XTHDCPD and NBD Hydrogenated Dimers

Addition of XTHDCPD to NBD hydrogenated dimers lowers the viscosity, the lowering being more pronounced the lower the temperature. This is illustrated in Fig. 7 by log η versus mole fraction of XTHDCPD isotherms for binary mixtures of HNN and XTHDCPD.

In terms of the best fit VTF equation parameters of Table VIII, the principal effect of adding XTHDCPD to the NBD hydrogenated dimers is to lower T_2. This expected in view of the previously mentioned dependence of T_2 on molecular weight[12]. As shown in Fig. 8, T_2 is within experimental error a linear function of mole fraction of XTHDCPD. The B parameters, on the other hand, are approximately the same for all mixtures. This suggested that the composition and temperature dependence of all mixtures of NBD hydrogenated dimers with XTHDCPD could be accounted for by a master viscosity equation of the form of Eq. (4) with constant

B and T_2 a linear function of XTHDCPD mole fraction. (Similar equations have been applied in the past to mixed hydrated salt melts[13].) A least squares fit of Eq. (4) to the data for all 21 compositions in Table XIII gave

$$T_2 = 153 - 58\, X_{XTHDCPD} \qquad (6a)$$

$$B = 819.0 \qquad (6b)$$

$$A_{HXX} = -7.466 \qquad (6c)$$

$$A_{HXN} = -7.137 \qquad (6d)$$

$$A_{HNN} = -7.043 \qquad (6e)$$

$$A_{PXtX} = -7.380 \qquad (6f)$$

$$A_{XTHDCPD} = -7.472 \qquad (6g)$$

$$\text{Std. Dev. } \ln \eta = 0.102 \qquad (6h)$$

Eq. (6a) is the least squares line through the data of Fig. 8. The solid lines in Fig. 7 have been calculated from Eqs. (4) and (6) and are a good example of the precision with which the master viscosity equation fits the data.

As before, the engineering significance of Eqs. (4) and (6) should be obvious. One may use these expressions to calculate with an average precision of 10% the viscosity of mixtures of NBD hydrogenated dimers and XTHDCPD over the entire 5-component composition range, a temperature range of -69 to 75°C, and a viscosity range of 0.013 to 20P.

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Table I. Molar enthalpies of fusion ΔH_f, pure compound melting points T_o, and impurity mol % 100 (1-X).

Compound	Formula	M(g/mol)	T_o(K)	ΔH_f (kcal/ mol)	100(1-X) by DSC	100(1-X) by VPC
HXX	$C_{14}H_{18}$	186.3	258.3 ± 0.2	3.69 ± 0.05	2.7 ± 0.2	1.4
HXN	$C_{14}H_{18}$	186.3	294.1 ± 0.7	1.80 ± 0.08	1.7 ± 0.2	2.8
HNN	$C_{14}H_{18}$	186.3	281.0 ± 0.2	5.24 ± 0.30	1.5 ± 0.1	3.2
PXtX	$C_{14}H_{20}$	188.3	336.8 ± 0.6	2.89 ± 0.13	2.2 ± 0.3	0.8
XTHDCPD	$C_{10}H_{16}$	136.2	$182._4$	1.1_1	$3._2$	4

Table II. Parameters for heat capacity equations c_p(cal/gK) = $c_p(T_o) + b[T(K) - T_o]$ for crystals and liquids

Compound		T range (K)	T_o (K)	$c_p(T_o)$	b	Std.Dev. c_p
HXX	(cryst)	211 to 243	285.3	0.280	0.00126	0.002
	(liq)	297 to 341		0.320	0.00126	0.004
HXN	(cryst)	208 to 261	294.1	0.297	0.00105	0.008
	(liq)	326 to 344		0.340	0.00105	0.002
HNN	(cryst)	214 to 250	281.0	0.262	0.00122	0.004
	(liq)	292 to 339		0.318	0.00122	0.006
PXtX	(cryst)	247 to 271	336.8	0.369	0.00141	0.005
	(liq)	344 to 384		0.381	0.00141	0.005
XTHDCPD	(liq)	210 to 340	182.4	0.254	0.00088	0.009

Table III. Comparison of crystal and liquid heat capacities at common temperatures.

cp(cal/gK)

Compound	Crystal @ 250K	Liquid @ 340K
HXX	0.236	0.389
HXN	0.251	0.388
HNN	0.224	0.390
PXtX	0.247	0.386
XTHDCPD	-----	0.393

Table IV. Comparison of observed melting points with those calculated for ideal solution behavior (Fig. 3)

Composition (mol fraction)	Highest Melting Component	m.p. (°C)			exp m.p. -calc.m.p.
		DSC	visual	calc.	
0.973 HXX-impurities	HXX	10.9	10.9	---	---
1.983 HXN-impurities	HXN	19.7	19.9	---	---
0.985 HNN-impurities	HNN	7.3	9.0	---	---
0.978 PXtX-impurities	PXtX	61.8	63.6	---	---
0.428 HXX-0.572 HXN	HXX	-29	---	-22	-7
0.562HXX-0.438 HNN	HXX	-17	---	-12	-5
0.312 HXX-0.490 HXN -0.198 HNN	HXX	-45	---	-33	-12
0.500 HXX-0.500 HNN	HNN	---	-21	-12	-9
0.358 HXX-0.321 HXN -0.321 HNN	HNN	---	-37	-23	-14
0.504 HNN-0.496 PXtX	PXtX	---	24	16	8
0.608 HXX-0.392 XTHDCPD	HXX	---	-9	-9	0
0.798 HXN-0.202 XTHDCPD	HXN	---	2	0	2
0.805 HNN-0.195 XTHDCPD	HNN	---	-8	1	-9
0.295 HNN-0.295 PXtX -0.410 XTHDCPD	PXtX	---	3	-13	16

Table V. Parameters for liquid density equations $\rho(g/cm^3) = \rho(0) - b'T(°C)$.

Composition (mol fraction)					T_{range}			
HXX	HXN	HNN	PXtX	XTHDCPD	(°C)	$\rho(0)$	$10^4 b'$	Std. Dev. ρ
1.000	---	---	---	---	10 to 70	1.092	7.7	0.001
---	1.000	---	---	---	-8 to 70	1.092	7.9	0.001
---	---	1.000	---	---	-41 to 70	1.104	7.6	0.001
---	---	---	1.000	---	65 to 75	1.038	7.8	0.002
---	0.504	0.496	---	---	-61 to 70	1.097	7.6	0.001
0.500	---	0.500	---	---	-22 to 72	1.100	8.4	0.001
---	---	0.504	0.496	---	25 to 75	1.071	7.5	0.001
0.358	0.321	0.321	---	---	-45 to 76	1.095	7.5	0.002
---	---	0.805	---	0.195	-50 to 55	1.092	7.4	0.002
---	---	0.594	---	0.406	-60 to 46	1.063	8.1	0.002
---	---	0.401	---	0.599	-56 to 55	1.033	7.9	0.002
---	---	0.196	---	0.804	-60 to 72	0.989	7.8	0.001
---	0.798	---	---	0.202	-25 to 70	1.070	8.6	0.002
---	0.601	---	---	0.399	-55 to 70	1.054	8.3	0.002
---	0.445	---	---	0.555	-65 to 70	1.016	7.9	0.001
---	0.200	---	---	0.800	-60 to 70	0.985	7.9	0.001
0.608	---	---	---	0.392	-50 to 70	1.051	7.6	0.001
---	0.308	0.301	---	0.391	-50 to 70	1.050	7.8	0.001
---	---	0.295	0.295	0.410	-20 to 70	1.028	8.1	0.001
0.247	0.222	0.221	---	0.310	-55 to 70	1.047	7.8	0.002
---	---	---	---	1.000	-70 to 75	0.950	7.7	0.002

Table VI. Comparison of densities of liquid XTHDCPD determined by various investigators.

	ρ (g/cm^3)				
T(^{o}c)	Ref.6	Ref.7	Ref.8	Ref.9	present work
-53.9	0.984	0.982	---	---	0.992
-40.0	0.975	0.973	---	---	0.981
-28.9	0.967	0.966	---	---	0.972
-6.7	0.953	---	---	---	0.955
15.6	---	---	0.939	0.936	0.938
23.9	---	0.934	---	---	0.932
29.4	0.929	---	---	---	0.927

Table VII. VTF equation parameters A and B and Std.Dev. $\ln\eta$ as a function of T_2 for the shear viscosity of HNN.

T_2	A	B	Std.Dev. $\ln\eta$
146	-7.300	894.5	0.009
148	-7.191	866.0	0.006
150	-7.081	837.8	0.009
152	-6.975	810.8	0.013

Table VIII. Best fit parameters for VTF equations for shear viscosity $\ln \eta\ (P) = A + B/[T(K) - T_2]$

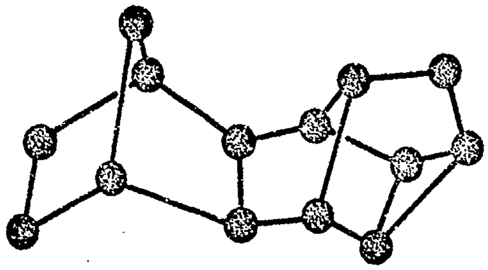
Composition (mol fraction)									
HXX	HXN	HNN	PXtX	XTHDCPD	T range (°C)	A	B	T_2	Std. Dev. ln η
1.000	---	---	---	---	0 to 70	-6.925	698.2	162	0.001
---	1.000	---	---	---	-5 to 70	-7.411	867.9	151	0.007
---	---	1.000	---	---	-41 to 70	-7.191	866.0	148	0.006
---	---	---	1.000	---	65 to 75	-7.526	854.4	150	0.002
---	0.504	0.496	---	---	-30 to 70	-7.218	849.7	150	0.004
0.500	---	0.500	---	---	-20 to 72	-7.079	783.6	155	0.015
---	---	0.504	0.496	---	25 to 75	-7.325	850.6	150	0.005
0.358	0.321	0.321	---	---	-35 to 76	-7.152	806.7	153	0.005
---	---	0.805	---	0.195	-50 to 55	-7.167	838.1	140	0.016
---	---	0.594	---	0.406	-60 to 46	-7.343	859.0	127	0.004
---	---	0.401	---	0.599	-56 to 55	-7.455	864.5	118	0.008
---	---	0.196	---	0.804	-60 to 72	-7.642	878.[illegible]	102	0.009
---	0.798	---	---	0.202	-25 to 70	-7.414	855.7	142	0.008
---	0.601	---	---	0.399	-55 to 70	-7.488	865.5	127	0.008
---	0.445	---	---	0.555	-65 to 70	-7.540	859.5	119	0.010
---	0.200	---	---	0.800	-60 to 70	-7.427	806.2	110	0.015
0.608	---	---	---	0.392	-45 to 70	-7.046	709.4	141	0.009
---	0.308	0.301	---	0.391	-50 to 70	-7.517	886.2	128	0.016
---	---	0.295	0.295	0.410	-20 to 70	-7.131	741.2	140	0.010
0.247	0.222	0.221	---	0.310	-55 to 70	-7.289	809.7	132	0.018
---	---	---	---	1.000	-69 to 75	-7.634	836.3	93	0.010

Table IX. Comparison of shear viscosities of XTHDCPD determined by various investigators.

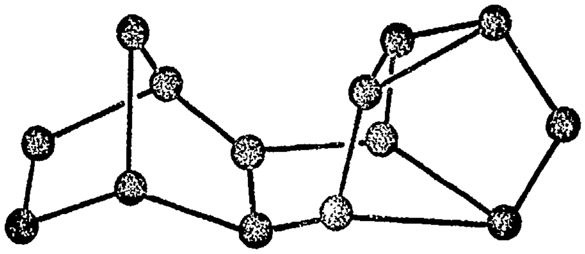
	η(P)				
T(°C)	Ref.6	Ref.7	Ref.8	Ref.9	present work
-53.9	0.297	0.32	0.359	---	0.363
-40.0	0.158	0.15	---	0.17	0.188
-31.7	---	---	0.127	---	0.135
-28.9	0.107	0.10	---	---	0.122
-27.8	---	---	---	0.085	0.117
-17.8	---	---	0.077	---	0.0834
-6.7	0.055	---	---	0.04	0.0600
10.0	---	---	0.051	---	0.0393
29.4	0.026	---	---	---	0.0261

Table X. Comparison of experimental viscosities with those calculated from Eqs(4) and (5) for commercial RJ-5 (0.2HXN - 0.7HNN - 0.1 PXtX).

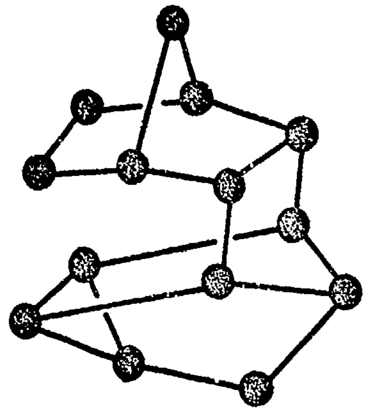
T(^{o}C)	η_{exp}(P)	η_{calc}(P)	η_{exp}/η_{calc}
80	0.0474	0.0480	0.99
50	0.0981	0.0994	0.99
20	0.274	0.278	0.99
0	0.714	0.726	0.98
-15	1.84	1.88	0.98
-30	6.39	6.53	0.98
-40	18.7	19.2	0.98
-50	72.9	74.8	0.97
-55	166	171	0.97



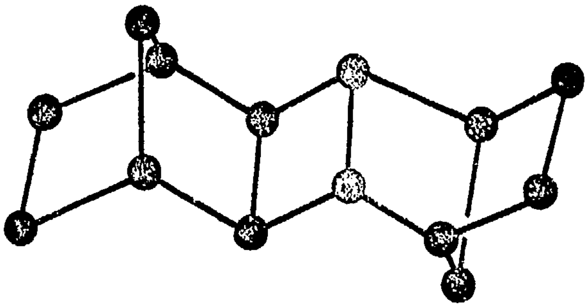
HXX



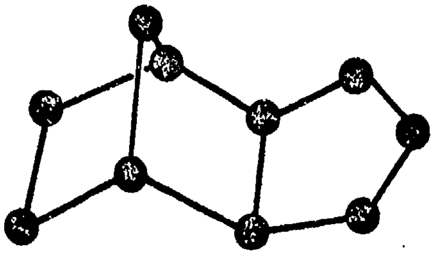
HXN



HNN



PXtX



XTHDCPD

Figure 1. Structures of compounds studied in the present paper: hexacyclic exo-exo-dihydrodinorbornadiene (HXX), hexacyclic endo-endo-dihydrodinorbornadiene (HNN), hexacyclic exo-endo-dihydrodinorbornadiene (HXN), pentacyclic exo-trans-exo-tetrahydrodinorbornadiene (PXtX), exo-tetrahydrodicyclopentadiene (XTHDCPC).

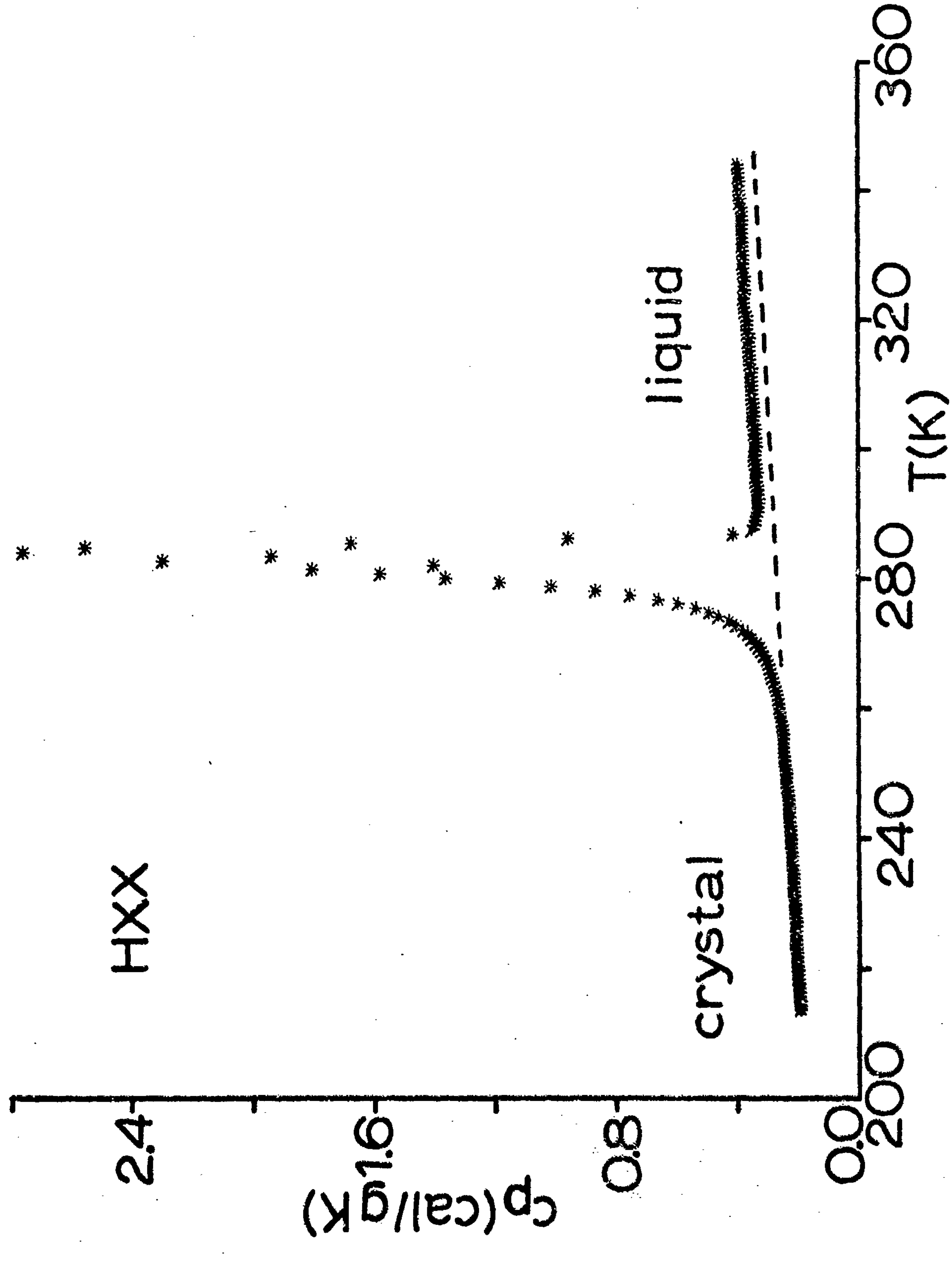


Figure 2. Heat capacity of a 15.72 mg sample of HXX measured at a heating rate of 5K/min above and below the fusion region.

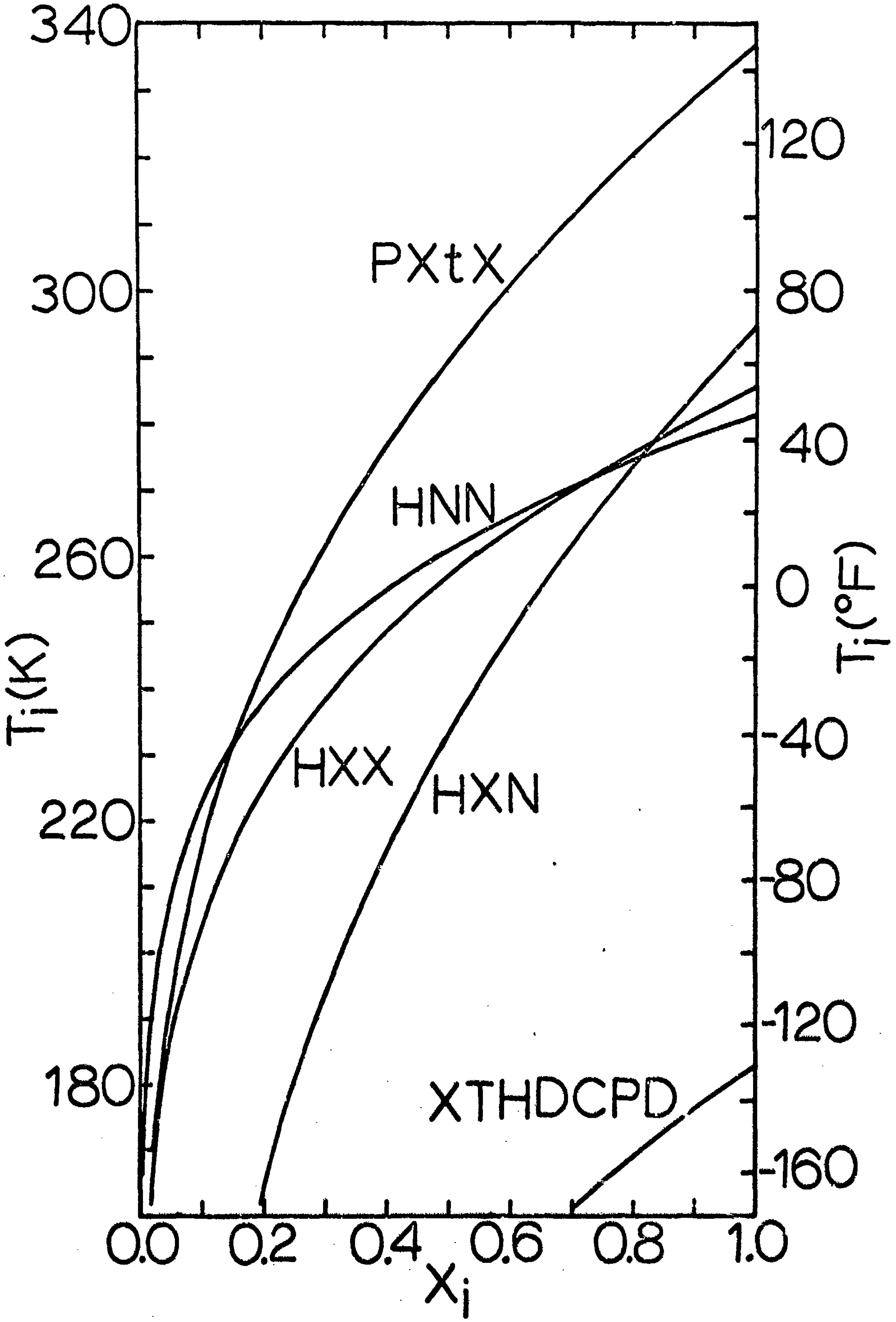


Figure 3. Ideal solution equilibrium freezing points T_i versus mole fraction X_i calculated from Eq. (1)

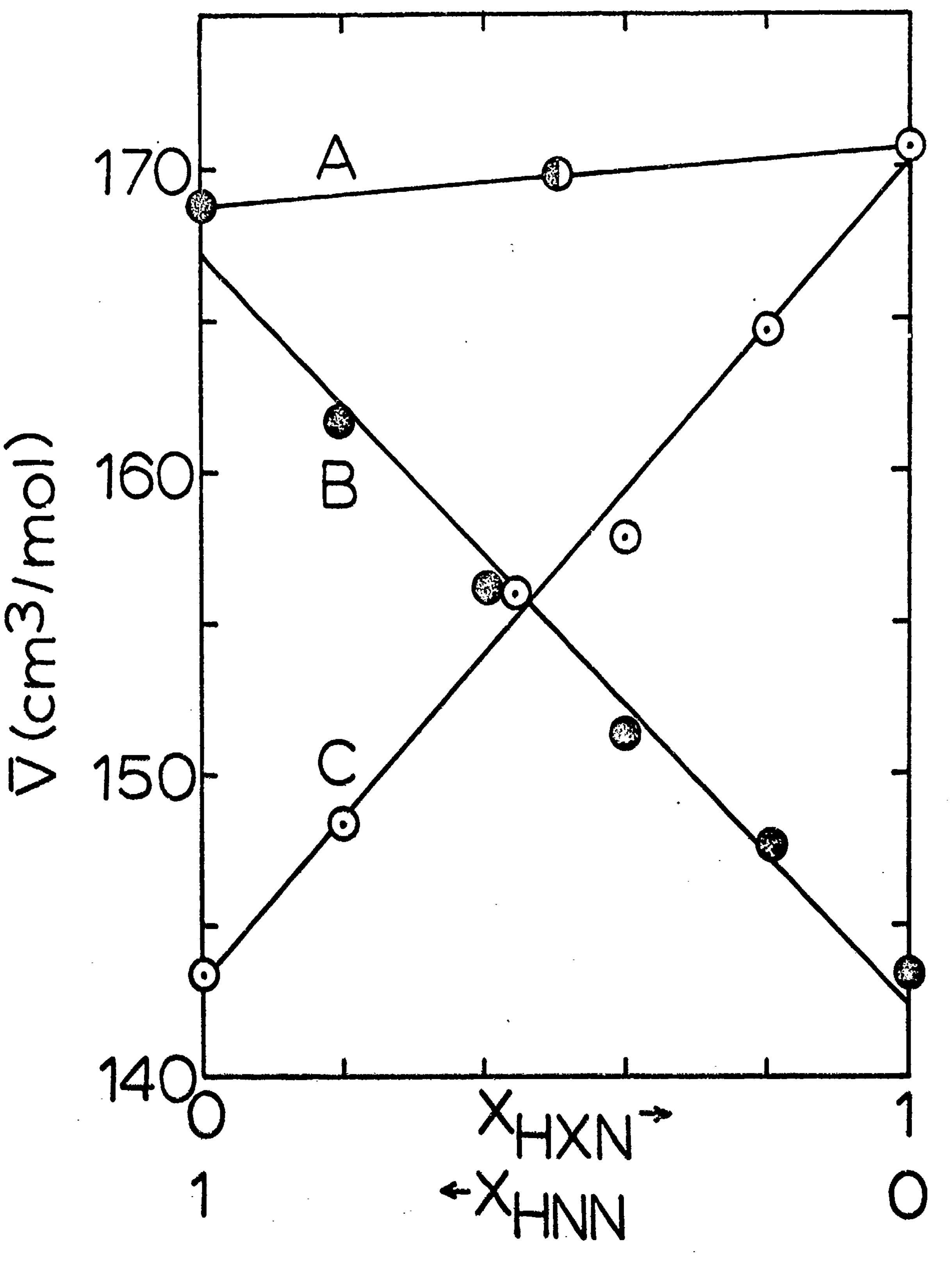


Figure 4. Molar volume at 0°C versus mole fraction for binary mixtures of (A) HXN-HNN, (B) HNN-XTHDCPD, and (C) HXN-XTHDCPD.

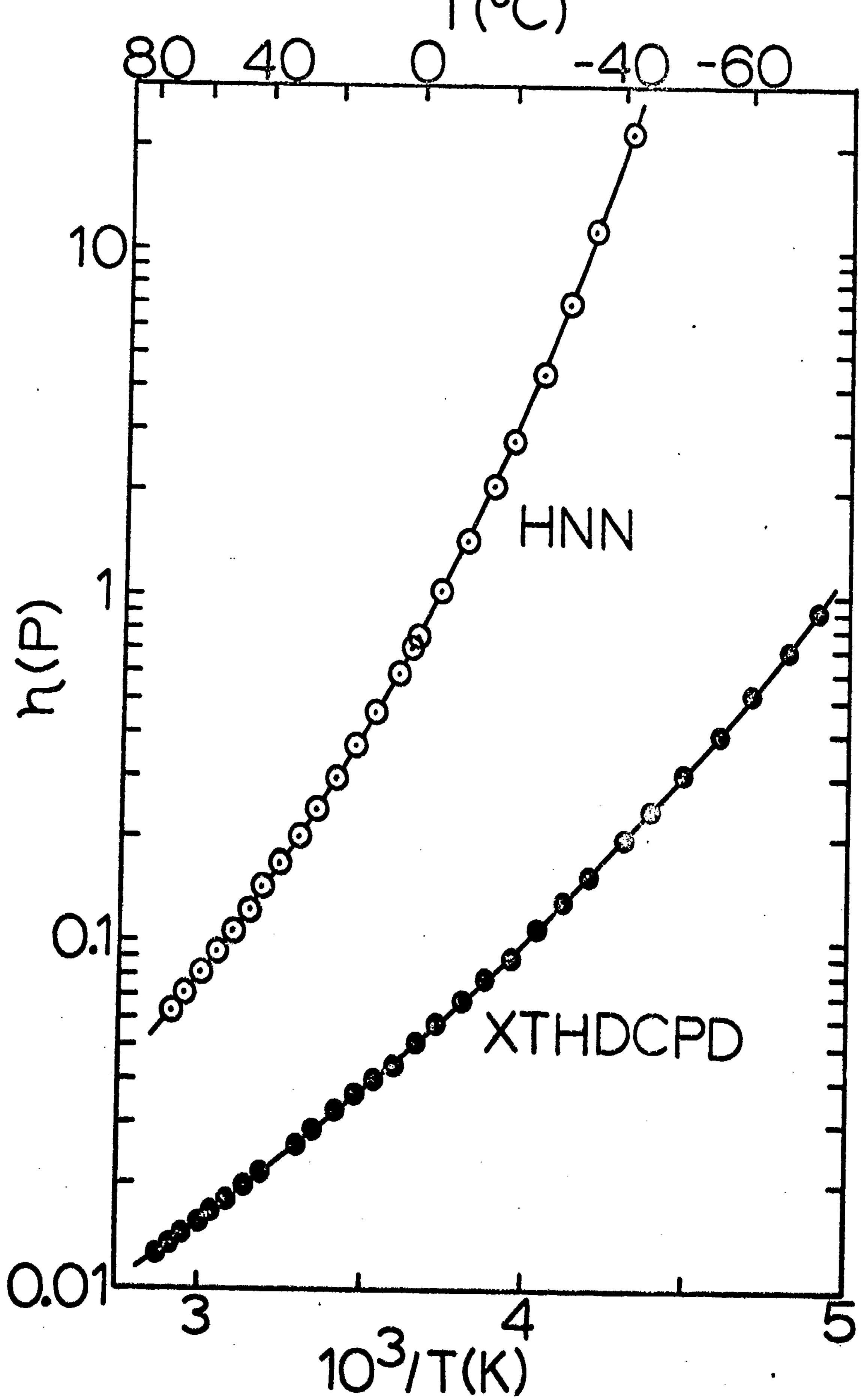


Figure 5. Arrhenius plots for the shear viscosities of HNN and XTHDCPD. Solid lines are best fits of the data to the VTF equation.

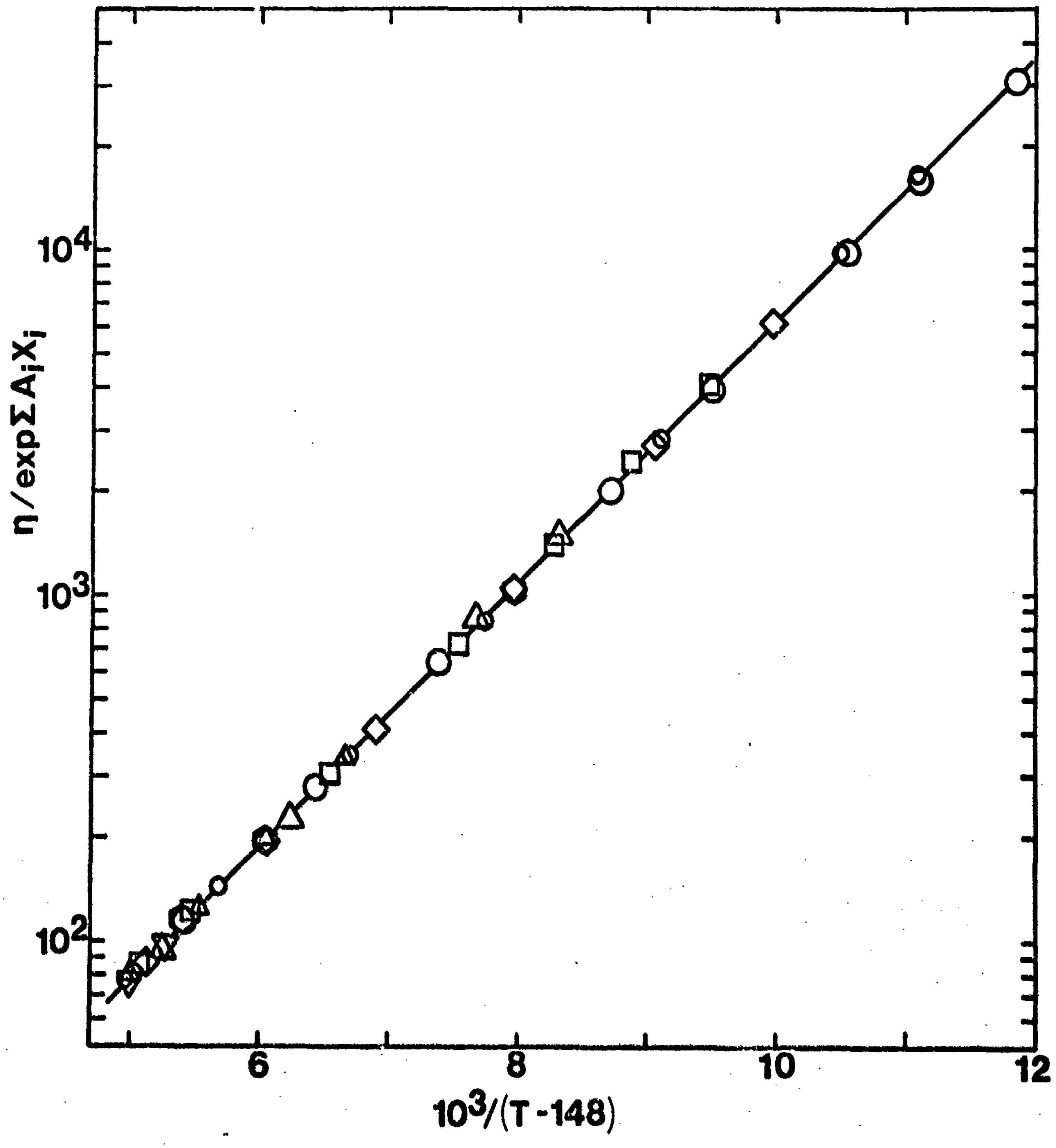


Figure 6. Master viscosity plot for mixtures of NBD hydrogenated dimers. Solid line is calculated from Eqs. (4) and (5). Compositions: ⬡ HXX, △ HXN, ○ HNN, ▽ PXtX, ◇ 0.504 HXN-0.496 HNN, □ 0.500 HXX -0.500 HNN, ▵ 0.504 HNN-0.496 PXtX, ◦ 0.358 HXX-0.321 HXN-0.321 HNN.

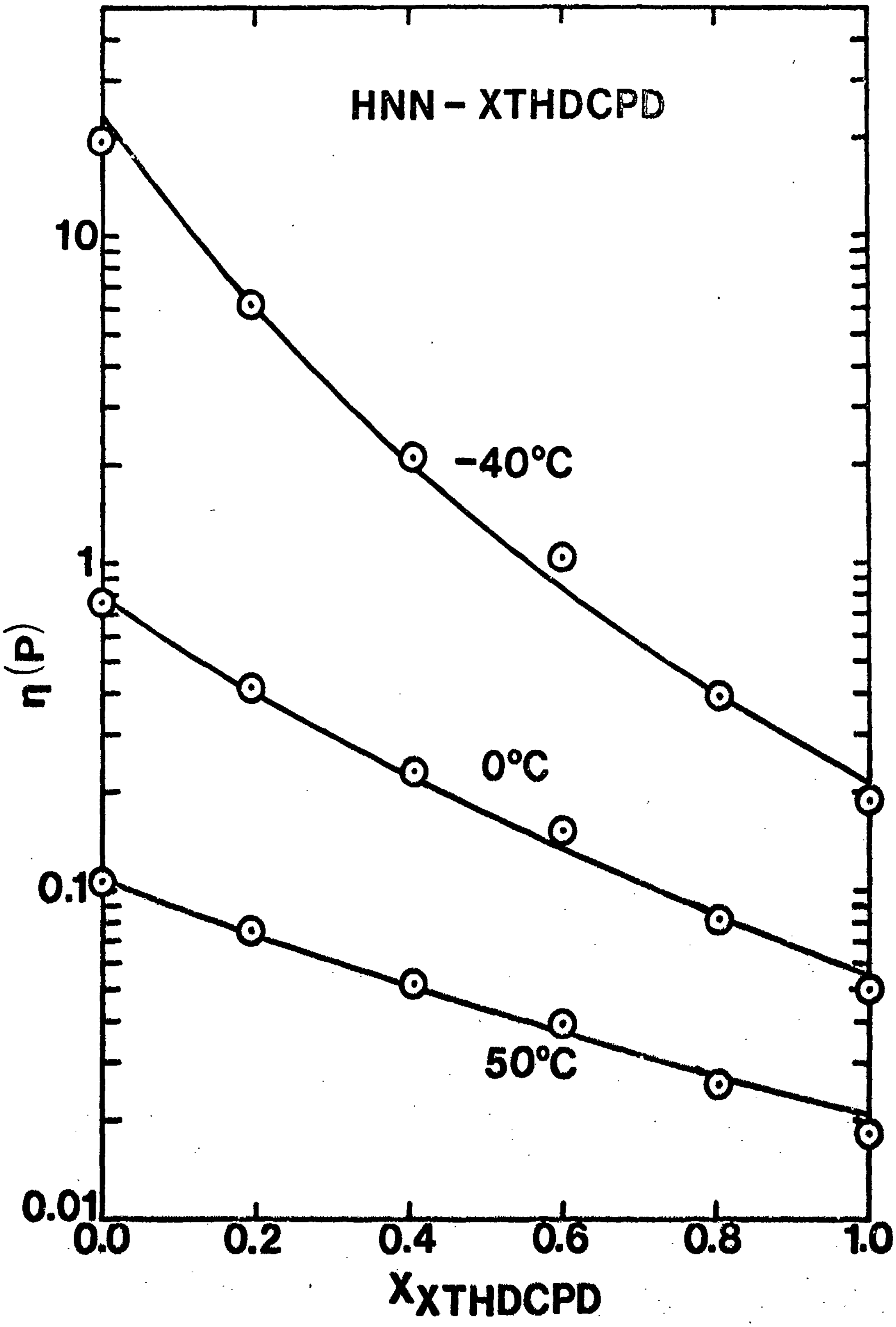


Figure 7. Viscosity isotherms for HNN-XTHDCPD mixtures. Solid lines are calculated from Eqs.(4) and (6).

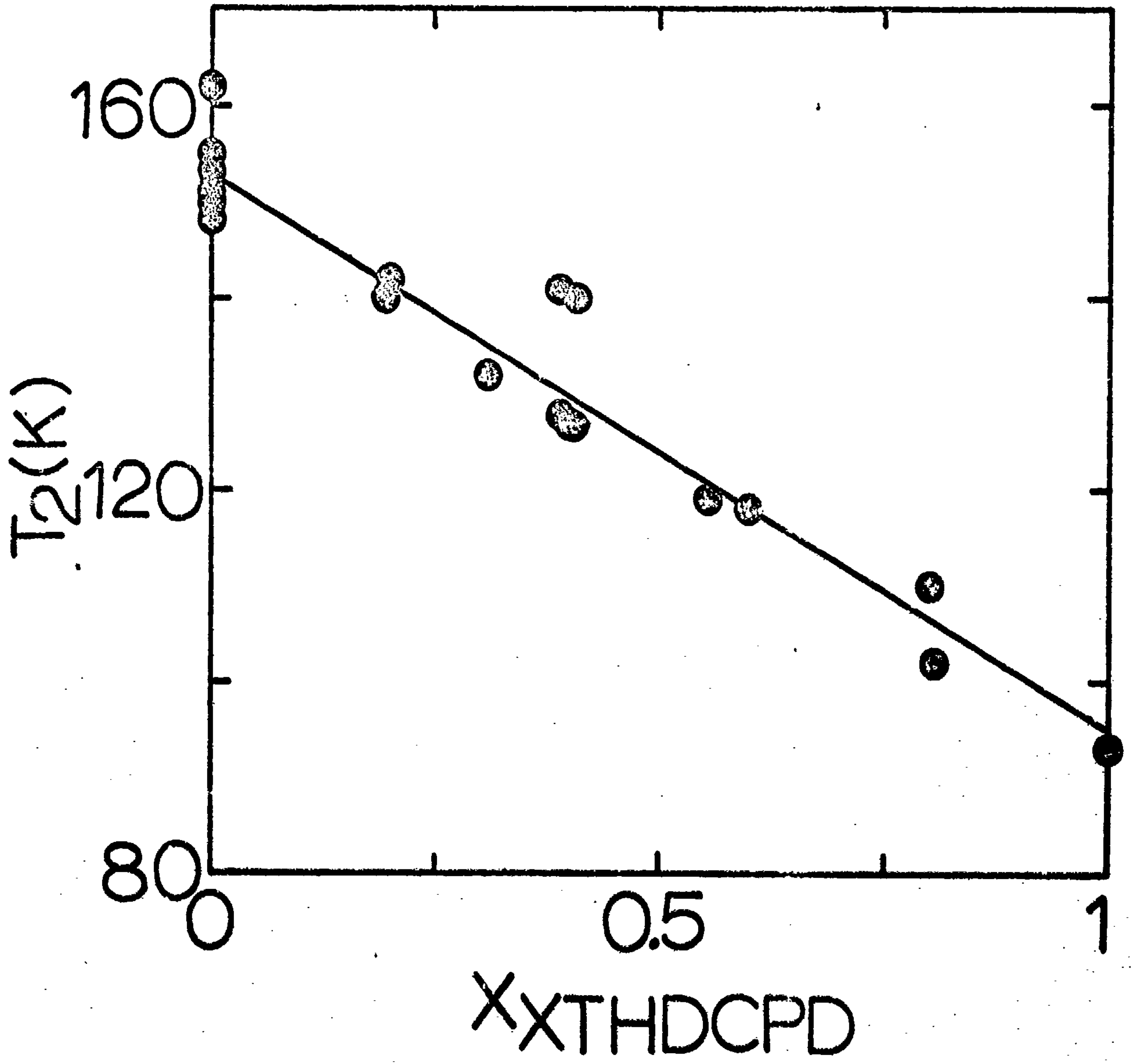


Figure 8. Best fit VTF equation T_2 parameters as a function of mole fraction of XTHDCPD.