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Effect of Pressure on the Phase Relations of Some *n*-Paraffins

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Abstract—The phase diagrams of n-$C_{21}H_{44}$, n-$C_{25}H_{52}$, n-$C_{22}H_{46}$, n-$C_{24}H_{50}$ and n-$C_{32}H_{66}$ were studied to 40 kbar by means of differential thermal analysis and volumetric techniques. n-$C_{21}H_{44}$ and n-$C_{25}H_{52}$ have orthorhombic/hexagonal/liquid triple points near 3 kbar, with the triple points marked by definite inflections in the melting curves. n-$C_{22}H_{46}$ transforms to a suspected monoclinic phase at ~2.6 kbar, 22 °C. It is concluded that even n-paraffins below n-$C_{22}H_{46}$ will all have similar high-pressure transformations. n-$C_{24}H_{50}$ has the triclinic/monoclinic transition at ~44 °C, 1 bar. The high-pressure melting curves of the even n-paraffins studied here all refer to the monoclinic phases, and are remarkably similar in slope and curvature, but have considerably less curvature than the orthorhombic odd n-paraffins. The monoclinic (or triclinic)/hexagonal/liquid triple points of the even n-paraffins studied are located at or below 1 kbar. The usual monoclinic phase of even n-paraffins above ~n-$C_{26}H_{54}$ is a high-pressure structure with respect to the usual triclinic phase of even n-paraffins below ~n-$C_{26}H_{54}$.

1. Introduction

Pure solid n-paraffins with nine or more carbon atoms in the chain crystallize in one or more of four definite structures. A hexagonal phase is stable just below the melting point for even n-paraffins between C_{22} and C_{44}, and for odd n-paraffins between C_9 and C_{43}.[1] The chains in this phase are arranged perpendicular to the plane formed by the methyl end groups, and they exhibit hindered rotation about their long axes.[2] The low-temperature phase of odd n-paraffins between C_9 and C_{43} and the only solid phase of odd n-paraffins above C_{43} are orthorhombic, space group D_{2h}^{11}-Pbcm.[3,4] The only solid phase of even n-paraffins between ~C_4 and C_{20} and the low-temperature phase of C_{22} are triclinic,[5,6] while the low-

temperature phase of C_{28} to C_{44} and the only solid phase of C_{46} and higher even n-paraffins are monoclinic.[7,8,9] C_{24} and C_{26} are known both in monoclinic and triclinic modifications.[3,10]

The odd–even differences can be explained in terms of packing differences of the end group layers.[7] The chains are tilted with respect to the methyl end group plane in all the low-temperature structures except the orthorhombic one. Small quantities of neighboring homolog impurities destroy the distinction between these low-temperature structures as well as the odd–even differences, and converts all these phases to an orthorhombic structure[3] which may, however, differ slightly from the orthorhombic structure of the pure odd n-paraffins.[11] Above $\sim C_{40}$ it becomes virtually impossible to prepare even n-paraffins in the monoclinic modification, but this can almost certainly be ascribed to the effect of small amounts of impurities.[7] A comprehensive review of the properties of the pure n-paraffins exists.[7]

The effect of pressure on the melting points and transition lines of several n-paraffin waxes (mixtures of neighboring homologs) has been studied to 40 kbar by Stokhuyzen and Pistorius.[12] Nelson *et al.*[13] measured the melting curves and transition lines of C_9, C_{12}, C_{13}, C_{15}, C_{18} and C_{24} to ~ 6 kbar. They found that the pressures of the triple points orthorhombic/hexagonal/liquid in the odd n-paraffins decrease with increasing carbon number. Kabalkina[14] reported transitions at 7.3 kbar to *less* dense phases for solid C_{30} and C_{32}, but this was doubted by other authors.[12]

Since the solid phases occurring in the waxes differ from those encountered in pure n-paraffins, a comparison of results between the pure and impure preparations would be of some interest. In addition, the odd–even difference only occurs in the pure substances, and the accurate work of Nelson *et al.*[13] did not cover a sufficient pressure range to give a clear indication of the difference in curvature of the melting curves of the odd and even members. Finally, the change from triclinic to monoclinic structures at $\sim C_{26}$ for the even numbers is not well understood.[7] Broadhurst[7] suggested that the end group packing may be an important factor in this change, but he was unable to show the relationship clearly in a phase diagram. In the case of the waxes it was shown[12] that increased pressure simulates increased mean carbon number. This suggests that a triclinic n-

paraffin, if compressed, may convert to a monoclinic high-pressure phase via an ordinary first-order transition.

2. Experimental

Samples of *n*-C_{21}, *n*-C_{22}, *n*-C_{24}, *n*-C_{25} and *n*-C_{32} with purities of better than 99% were obtained from Rare Chemicals Ltd, Norfolk, England.

Pressures up to 40 kbar were generated in a piston-cylinder apparatus.[15] High-temperature phase changes were studied by means of DTA, using Chromel–Alumel thermocouples. Heating/cooling rates ranged from 0.2–1.5 °C/sec. The detailed experimental procedure has been described before.[16] The final pressures are believed to be accurate to ± 0.5 kbar. The samples were contained in stainless steel or copper capsules, pre-sealed *in situ* at ~ 16 kbar. Melting curves were obtained only from points upon heating, but cooling points were usually in good agreement unless supercooling occurred.

3. Results

n-$C_{21}H_{44}$

The phase diagram of C_{21} is shown in Fig. 1. Melting and freezing of C_{21} I and II yielded strong DTA signals at low pressures (Fig. 2(i)). At higher pressures the signals became smaller, but remained clear. Above ~30 kbar signal strength increased once more. The II/I transition was not directly observed at elevated pressure, but a change in the slope of the melting curve marked the II/I/liquid triple point at 2.4 kbar, 82.5 °C. This requires a mean slope of 20.5 °C/kbar for the II/I transition line. The melting curve of C_{21} I rises with an initial slope of 21 °C/kbar to the II/I/liquid triple point, where the slope of the melting curve of C_{21} I is ~ 14 °C/kbar. The initial slope of the melting curve of C_{21} II at this point is 17.7 °C/kbar. The melting curve of C_{21} II was followed to 33.6 kbar, 323.5 °C. The phase relations of C_{21} are summarized in Table 1, with the melting curves fitted to the Simon equation[17]

$$(P - P_0)/A = (T/T_0)^c - 1$$

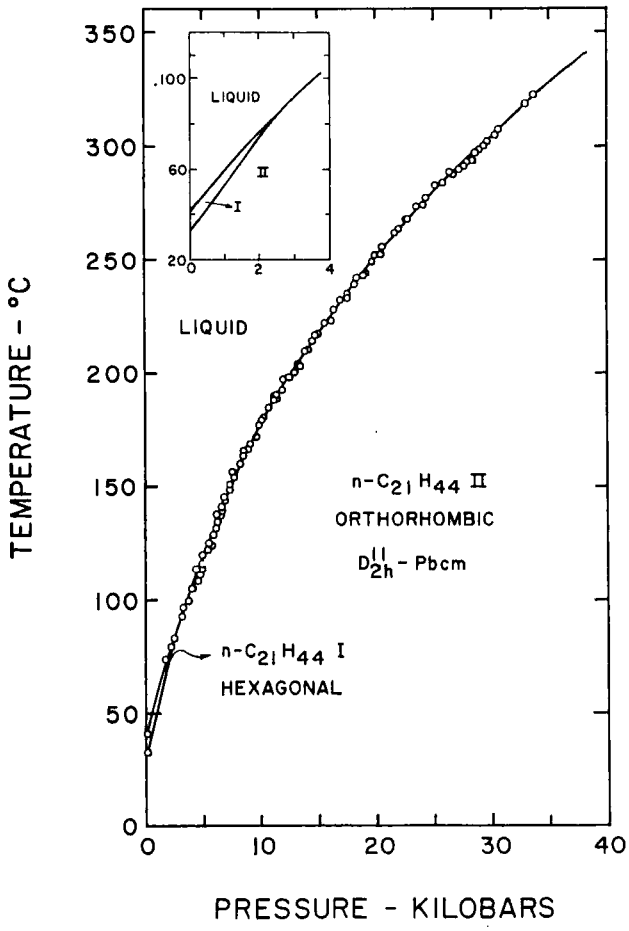

Figure 1. Phase diagram of n-$C_{21}H_{44}$ to 40 kbar.

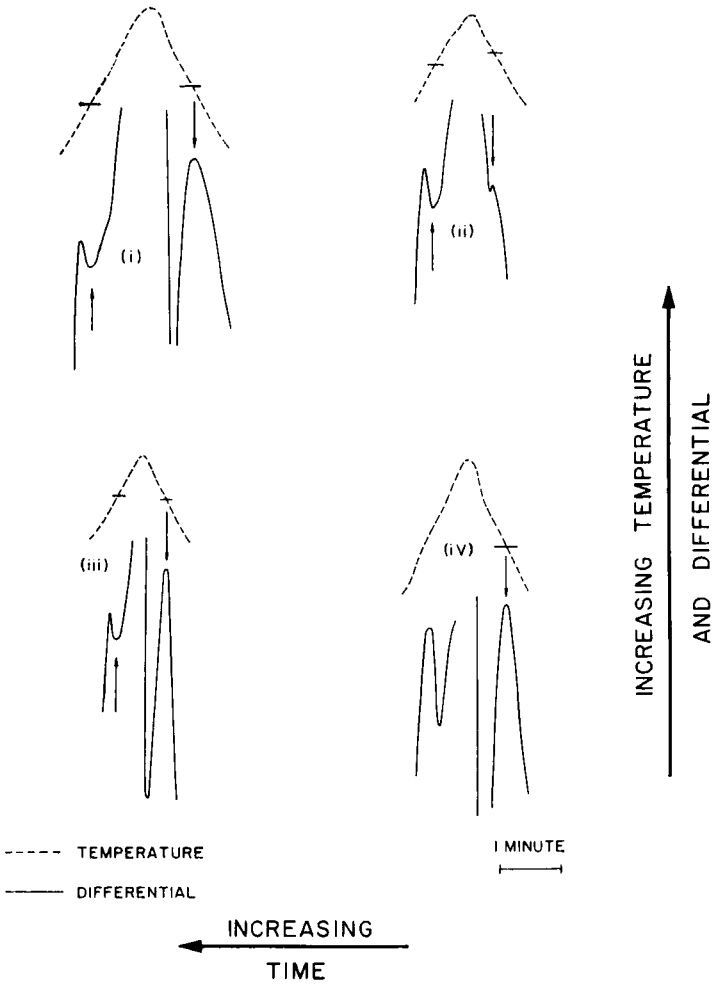

Figure 2. Typical DTA signals obtained. (i) C_{21} II/liq at 3.5 kbar, 101.6 °C heating, 90.6 °C cooling; (ii) C_{22} III/liq at 35.4 kbar, 366.8 °C heating, 363.5 °C cooling; (iii) C_{24} II/liq at 25.9 kbar, 323.1 °C heating, 324.1 °C cooling; (iv) C_{25} II/liq at 14.1 kbar, 232.1 °C heating.

TABLE 1 Phase Relations of the *n*-paraffins

Phase Boundary	Fit	Standard deviation
C_{21} II/I[a]	$t(°C) = 32.5 + 20.5P$	—
C_{21} I/liq[b]	$t(°C) = 40.2 + 21P - 1.5P^2$	—
C_{21} II/liq	$(P\text{-}2.4)/5.428 = (T/355.8)^{3.708} - 1$	2.1 °C
C_{25} II/I[a]	$t(°C) = 47.0 + 19.7P$	—
C_{25} I/liq[b]	$P/6.065 = (T/326.7)^{2.579} - 1$	0.3 °C
C_{25} II/liq	$(P\text{-}3.6)/5.701 = (T/391.6)^{4.040} - 1$	1.5 °C
C_{22} II/I[c]	$t(°C) = 43 + 25P$	—
C_{22} I/liq[c]	$t(°C) = 44 + 23P$	—
C_{22} II/liq[c]	$t(°C) = 58 + 24.4(P\text{-}0.6)$	—
C_{22} III/liq	$(P\text{-}0.8)/3.832 = (T/336.2)^{3.582} - 1$	2.0 °C
C_{22} II/III[c]	$P \simeq 4 - 0.05t(°C)$	—
C_{24} III/II[d]	$t(°C) \simeq 44 - 20P$	—
C_{24} II/I[e]	$t(°C) = 48.1 + 28.7P$	—
C_{24} I/liq[e]	$t(°C) = 50.3 + 25.3P - 1.6P^2$	—
C_{24} II/liq[f]	$(P\text{-}0.5)/3.998 = (T/337)^{3.493} - 1$	1.3 °C
C_{32} II/I[a]	$t(°C) = 65.5 + 21.2P$	—
C_{32} I/liq[a]	$t(°C) = 69.3 + 17.3P$	—
C_{32} II/liq	$(P\text{-}1.0)/5.193 = (T/359.2)^{3.428} - 1$	1.4 °C

Triple point	Pressure[g] (kbar)	Temperature[g] (°C)
C_{21} II/I/liq	2.4	82.5
C_{25} II/I/liq	3.6	118.5
C_{22} II/I/liq[c]	0.6	58
C_{22} III/II/liq[c]	0.8	63
C_{24} II/I/liq	0.5	64
C_{24} II/III/I[h]	- 0.1	47
C_{32} II/I/liq	1.0	86

[a] Linear interpolation between atmospheric pressure transition point and triple point.

[b] Few points observed. Fit is more or less formal.

[c] These values are given under the assumption of a III/II/liquid triple point at 0.8 kbar and a II/I/liquid triple point at 0.6 kbar. It is possible that the II/III boundary may intersect the II/I boundary before it reaches the melting point, in which case III/I/liquid and III/II/I triple points will occur instead. These fits are given mainly to clarify possible phase relations, and should not be used for quantitative purposes.

[d] Atmospheric pressure point from Ref. 10 and slope taken to be the same as the estimated value for C_{22} II/III.

[e] From Ref. 13.

[f] Fit based on present points as well as points from Ref. 13.

[g] The accuracy of these points can be judged best by references to the figures.

[h] Estimated values.

TABLE 2 Thermodynamic Parameters for the *n*-paraffins

Phase change	Pressure (kbar)	Slope[a] (°C/kbar)	Entropy change[b] (J/mole-deg)	Volume change[c] (cm³/mole)
n-$C_{21}H_{44}$ I/liq	0.001	~21	152	~32
	2.4	14	~152[d]	~21.3
n-$C_{21}H_{44}$ II/I	<2.4	20.5	50.6	10.4
n-$C_{21}H_{44}$ II/liq	2.4	17.7	~202.6[e]	~35.9
n-$C_{25}H_{52}$ I/liq	0.001	20.9	177	37
	3.6	15.7	~177[d]	~28
n-$C_{25}H_{52}$ II/I	<3.6	19.7	81.4	16
n-$C_{25}H_{52}$ II/liq	3.6	17.0	~258[e]	~44
n-$C_{22}H_{46}$ II/I	< ~0.6	~25	89	~22
n-$C_{22}H_{46}$ I/liq	< ~0.6	~23	154	~36
n-$C_{22}H_{46}$ II/liq	~0.6	~24.4	~243[e]	~59
n-$C_{22}H_{46}$ II/III	~2.6	−12 to −19[h]	~7[f]	−0.8 to −1.3[g]
n-$C_{22}H_{46}$ III/liq	0.8	24.5	~236[e]	~58
n-$C_{24}H_{50}$ III/II	0.001	~ −20[i]	~7[i]	~ −1.4
n-$C_{24}H_{50}$ II/I	<0.5	28.7	97	28
n-$C_{24}H_{50}$ I/liq	0.001	25.3	~170	43
	0.5	23.7	~170[d]	~40
n-$C_{24}H_{50}$ II/liq	0.5	24.2	~267[e]	~65
n-$C_{32}H_{66}$ II/I	<1.0	~21.2	~115[j]	~25
n-$C_{32}H_{66}$ I/liq	<1.0	~17.3	224	~39
n-$C_{32}H_{66}$ II/liq	1.0	20.2	~339[e]	~68

[a] Observed values.
[b] Taken from Ref. 7.
[c] Calculated from previous two columns by use of the Clapeyron–Clausius equation.
[d] Value on the assumption that ΔS does not change much along the short melting curve.
[e] From the additive relations at the triple point.
[f] Value estimated for the triclinic/monoclinic transition on the basis of extrapolation of curves of $\Delta H_{\text{triclinic/liq}}$ and $\Delta H_{\text{monoclinic/liq}}$ from Ref. 7.
[g] Present experimental values, of which −1.3 cm³/mole is judged the more probable one.
[h] Range of values calculated from the following two columns by use of the Clapeyron–Clausius equation.
[i] These values assumed to be closely the same as in the case of the n-$C_{22}H_{46}$ II/III transition.
[j] Estimated value on basis of other data in Ref. 7.

where P_0 and T_0 are the coordinates of the triple point of the phase in question, and A and c are adjustable parameters, determined by means of Babb's method.[18] Some thermodynamic parameters, deducible from the observed slopes and the known entropy changes, are collected in Table 2.

n-$C_{25}H_{52}$

The phase diagram of C_{25} is shown in Fig. 3. A DTA signal typical of the melting and freezing both of C_{25} I and II is shown in Fig. 2(iv). The II/I transition was once again not directly observed at elevated pressure, but a change in the slope of the melting curve marked the II/I/liquid triple point at 3.6 kbar, 118.5 °C. This requires a mean slope of 19.7 °C/kbar for the II/I transition line. The melting curve of C_{25} I rises with an initial slope of 20.9 °C/kbar to the II/I/liquid triple point, where its slope is 15.7 °C/kbar. The initial slope of the melting curve of C_{25} II at this point is 17.0 °C/kbar. The melting curve of C_{25} II was followed to 34.9 kbar, 351.3 °C. The phase relations of C_{25} are summarized in Table 1, and some thermodynamic parameters in Table 2.

n-$C_{22}H_{46}$

Possible high-pressure polymorphism of C_{22} was studied by volume-discontinuity techniques, previously described by Pistorius and Clark.[16] At 22 °C indications of a phase change C_{22} II/III at 2.6 ± 0.8 kbar were observed. The volume change in our first experiment was found to be 0.4% or 1.3 cm³/mole, but a repetition with the same sample, left overnight, yielded a volume change of only 0.25% or 0.8 cm³/mole. It appears probable that the transition is rather sluggish. Our probable experimental uncertainty is $\sim 0.1\%$, and the reality of the transition is therefore not established beyond all doubt, but is nevertheless considered to be highly probable. A typical compression curve, uncorrected for friction, is shown in Fig. 4.

The internally-heated piston-cylinder apparatus is not well adapted for measurements on melting curves below ~ 1.5 kbar. Our first high-pressure point was taken at 1.3 kbar, and, judging from the work of Nelson *et al.*[13] on C_{24}, this is already beyond the limit of stability of hexagonal C_{22} I. For the purpose of fitting the

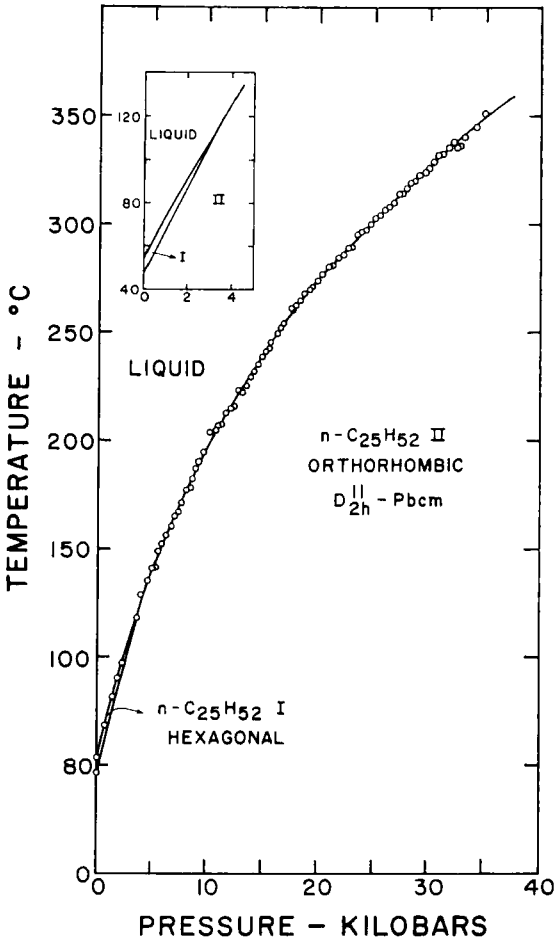

Figure 3. Phase diagram of n-$C_{25}H_{52}$ to 40 kbar.

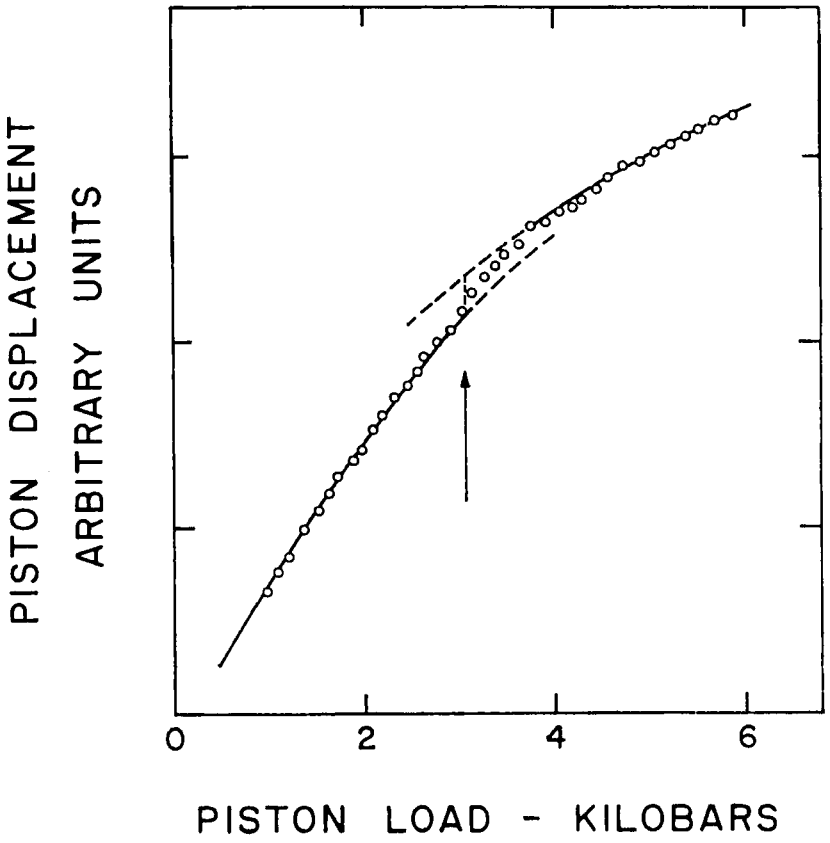

Figure 4. Typical compression curve showing the suspected high-pressure transition of n-$C_{22}H_{46}$ at 22 °C.

curves, the II/I/liquid triple point was arbitrarily fixed at 0.8 kbar, 63.0 °C, thus allowing the melting curve of C_{22} II(III) to extrapolate to 1 bar at a temperature between the known II/I and I/liquid temperatures. The phase diagram of C_{22} is shown in Fig. 5. As it will appear below in the discussion, it is probable that all melting signals observed by us refer to C_{22} III, and in any case the melting curve of C_{22} II, if it occurs, should have closely the same slope as that of C_{22} III. The melting signals were broader than usual at low pressures, but become stronger and sharper at higher pressures. A typical DTA signal is shown in Fig. 2(ii). The melting curve of C_{22} III was followed to 35.4 kbar, 366.3 °C.

The phase relations of C_{22} are summarized in Table 1, and some thermodynamic parameters in Table 2.

n-$C_{24}H_{50}$

The phase diagram of C_{24} is shown in Fig. 6. Nelson *et al.*[13] found the stability range of hexagonal C_{24} I to be terminated at 0.6 kbar, 64.0 °C. Mazee[10] found that triclinic C_{24} III, stable at ordinary conditions, transforms to monoclinic C_{24} II at 1 bar, 46 °C upon heating. This sluggishly reverts to C_{24} III below ~42 °C upon cooling. If, as will be shown later, this triclinic/monoclinic transformation is the counterpart of the C_{22} II/III transition, the triple point found by Nelson *et al.*[13] must be the C_{24} monoclinic (II)/hexagonal(I)/liquid triple point, and not, as they assumed, the triclinic/hexagonal/liquid triple point.

The melting curve of C_{24} II yielded strong DTA signals (Fig. 2(iii)). The agreement between the present points and those of Nelson *et al.*[13] to 4.4 kbar is extremely good, as shown in Fig. 6. The initial slope of the melting curve of C_{24} II is 24.6 °C/kbar. The melting curve was followed to 35.8 kbar, 376.1 °C. The phase relations of C_{24} are summarized in Table I, and some thermodynamic parameters in Table 2.

n-$C_{32}H_{66}$

The phase diagram of C_{32} is shown in Fig. 7. No pressure melting points were taken below 1 kbar, and this proved to be above the II/I/liquid triple point. The triple point is arbitrarily taken as 1 kbar, 86 °C, but this value is merely an upper limit. Clear and sharp

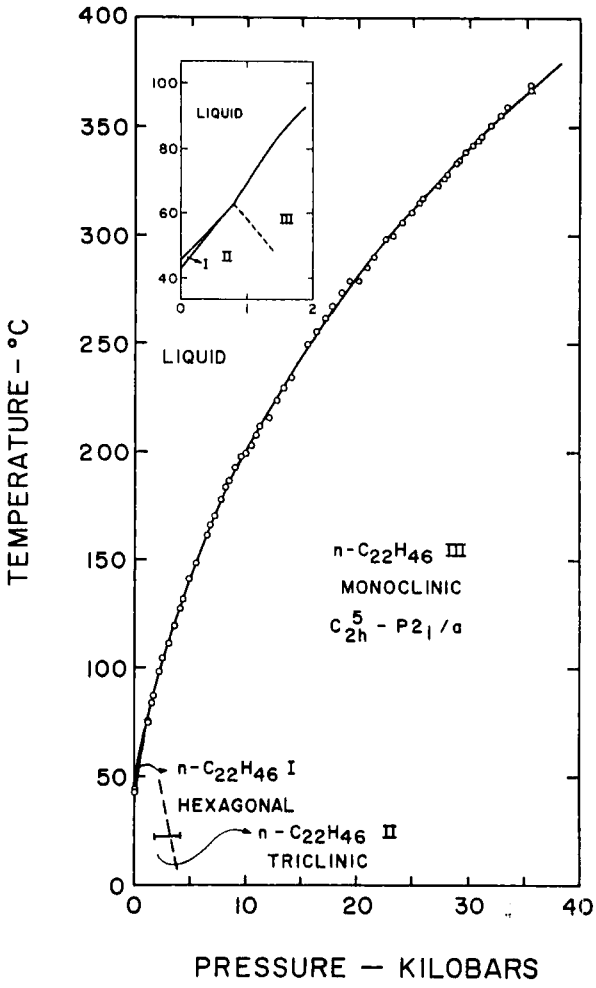

Figure 5. Phase diagram of n-$C_{22}H_{46}$ to 40 kbar.

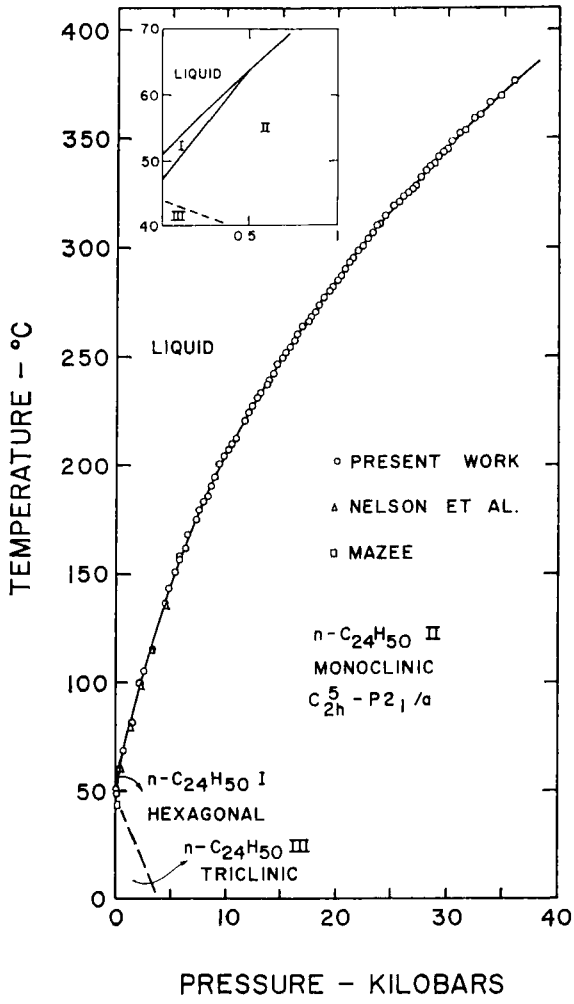

Figure 6. Phase diagram of n-$C_{24}H_{50}$ to 40 kbar.

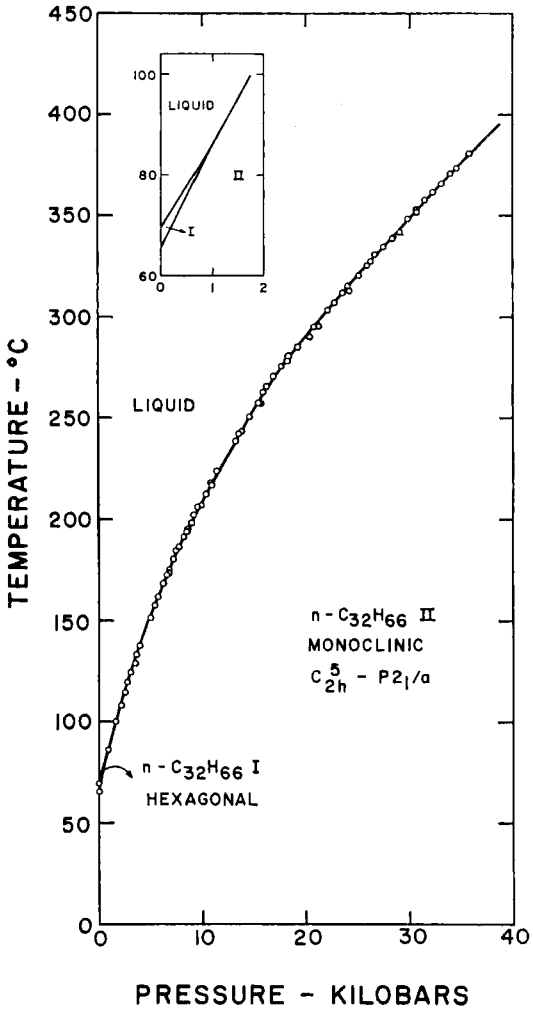

Figure 7. Phase diagram of n-$C_{32}H_{66}$ to 40 kbar.

DTA signals were obtained upon melting and freezing C_{32} II. The initial slope (at 1 kbar) of the melting curve of C_{32} II is 20.2 °C/kbar. The melting curve was followed to 35.7 kbar, 380.8 °C. The phase relations of C_{32} are summarized in Table 1, and some thermodynamic parameters in Table 2.

4. Discussion

Broadhurst[7] concluded that the frequent occurrence of the orthorhombic structure in even n-paraffins above $\sim C_{40}$ is probably due to impurities and the very small difference in free energy between the orthorhombic and monoclinic phases. The monoclinic phase appears to be the stable one in the case of pure material even up to C_{94}.[9]

Broadhurst[7] further stated that " it is more puzzling that in pure paraffins the triclinic phase is not observed above $\sim C_{26}$ while the monoclinic phase is not observed below ". The answer to this question can apparently only be found in the pressure behavior of these substances. Stokhuyzen and Pistorius[12] found that most of the phase properties of impure n-paraffins behave in the same way when increasing pressure as when increasing mean carbon number. Since the monoclinic phase appears at high carbon numbers, this suggests that, for lower carbon numbers, the triclinic phase will transform to a monoclinic one at elevated pressures. If this is the case, the monoclinic phase must be denser than the triclinic one for any given n-paraffin. Unfortunately no accurate density determinations appear to be available for C_{26}, but in the case of C_{24}, where the triclinic phase converts to the monoclinic modification at ~ 44 °C at atmospheric pressure,[10] the monoclinic phase is in fact $\sim 0.8 \pm 0.6\%$ denser than the triclinic phase. Extrapolation of the plots of enthalpy of fusion versus carbon number[7] for the n-paraffins indicate that, at carbon numbers near C_{24}, the enthalpy of fusion of the triclinic phase is higher than that of the corresponding monoclinic phase by an amount which corresponds to $\Delta S_{\text{triclinic/monoclinic}} \simeq 7$ J/mole-deg. This means that, in the $P - T$ plane, the triclinic/monoclinic transition line should have a negative slope, and that the monoclinic phase should therefore be a high-pressure high-temperature phase with respect to the triclinic phase. In the case of C_{22} we

observed a high-pressure transition with a volume change of $\sim 0.4\%$, which, in view of the above considerations, must be ascribed to the phase change from triclinic to monoclinic. The transition appeared to be rather sluggish, in agreement with the results on C_{24}[10] and with the fact that for C_{26}, where we suspect that the transition temperature between triclinic and monoclinic is quite close to room temperature, both phases can be obtained at ordinary conditions.

The model presented above implies that for C_{28} and higher the triclinic phase will only occur at low temperatures, where the rate of transition may be prohibitively low. Nevertheless, it may be possible to crystallize triclinic phases of C_{28} and higher even *n*-paraffins from suitable solvents at very low temperatures. In the case of C_{20} and lower even *n*-paraffins the monoclinic phase will appear as a high-pressure phase. The transition pressure will increase with lower carbon number.

The question arises why Nelson *et al.*[13] did not detect the monoclinic/triclinic/liquid triple point in their high-pressure study of C_{18}. It can be accepted that the change of slope of the melting curve will be negligible. However, if one plots their values of the volume change upon melting versus pressure, the slopes of these lines show rather marked inflections near 2 kbar for C_{18} and ~ 5 kbar for C_{12}, while in the case of C_{24} the slope $d\Delta V/dP$ is rather similar to that of C_{18} above 2 kbar, suggesting that the triple point found by Nelson *et al.*[13] at ~ 0.5 kbar, 64 °C is, as assumed in the present work, the monoclinic/hexagonal/liquid triple point.

The slopes and curvatures of the melting curves of C_{21} and C_{25} can be almost perfectly matched by shifting the two curves relative to each other by ~ 20 °C and 0.5 kbar. However, it is not possible to match these melting curves with the melting curves of the even *n*-paraffins studied, although the melting curves of the even homologs can easily be matched against each other by slight shifts.

In the majority of cases the present slopes of the curves below ~ 2 kbar are not well determined, but, nevertheless, the agreement in Table 2 between the initial volume change upon melting of the low-temperature phase and the sum of the volume changes of the low–high transition and the melting of the high-temperature phase is good in all cases. This agreement is a sensitive check on the essential correctness of the slopes near the triple points.

Nelson *et al.*[13] found that their accurate melting curves could be satisfactorily fitted to the Simon equation only in the case of C_{18}. The present work is rather less accurate, but covers a much greater range of pressures. Our curves could in all cases be satisfactorily fitted to the two-parameter Simon equation, resulting in lower standard deviations than for four-parameter power series. Kennedy[19] has stated that the Simon equation can be expected to describe the melting behavior of Van der Waals solids reasonably well, but has expressed doubts on the applicability of this equation to ionic substances and metals. Nevertheless, even for such materials the equation may be convenient as a formal interpolation equation.

In the case of the impure n-paraffin waxes[12] the investigations were considerably hampered by failure of the samples to recrystallize fully upon freezing. It was often necessary to anneal the samples at temperatures below the melting point in order to regain strong DTA signals. A slight tendency to a similar effect was here found for C_{21}, but in general the samples melted and froze sharply, with no tendency to a decrease in crystallinity.

The orthorhombic/hexagonal/liquid triple points of the waxes are located at considerably higher pressures than the corresponding triple points of the pure odd n-paraffins of roughly the same carbon number, and the low-temperature/hexagonal/liquid triple points of the pure even n-paraffins studied here and by Nelson *et al.*[13] are located at even lower pressures. This can be considered a further indication that the orthorhombic structure of the waxes is crystallographically different from the orthorhombic structure of the pure odd n-paraffins, as claimed by Stokhuyzen.[11]

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REFERENCES

1. Müller, A., *Proc. Roy. Soc.* (London) **127**, 417 (1930).
2. Hoffmann, J. D. and Decker, B. F., *J. Phys. Chem.* **57**, 520 (1953).
3. Smith, A. E., *J. Chem. Phys.* **21**, 2229 (1953).
4. Vand, V., *Acta Cryst.* **6**, 797 (1953).
5. Norman, N. and Mathisen, H., *Acta Cryst.* **13**, 1043 (1960).
6. Müller, A. and Lonsdale, K., *Acta Cryst.* **1**, 129 (1948).
7. Broadhurst, M. G., *J. Res. NBS* **66A**, 241 (1962).
8. Schaerer, H. M. M. and Vand, V., *Acta Cryst.* **9**, 379 (1956).
9. Passaglia, E., private communication quoted in ref. 7.
10. Mazee, W. M., *Rec. Trav. Chim. Pays-Bas.* **67**, 197 (1948).
11. Stokhuyzen, R., Thesis, Rhodes University (1969).
12. Stokhuyzen, R. and Pistorius, C. W. F. T., *J. Appl. Chem.* **20**, 1 (1970).
13. Nelson, R. R., Webb, W. and Dixon, J. A., *J. Chem. Phys.* **33**, 1756 (1960).
14. Kabalkina, S. S., *Dokl. Akad. Nauk SSSR* **125**, 114 (1959).
15. Kennedy, G. C. and LaMori, P. N., in *Progress in Very High Pressure Research*, Bundy, F. P., Hibbard, W. R., Jr., and Strong, H. M., Eds. (John Wiley & Sons, Inc., New York, 304, 1961).
16. Pistorius, C. W. F. T. and Clark, J. B., High Temperatures–High Pressures **1**, 561 (1969).
17. Simon, F. E. and Glatzel, G., *Z. Anorg. Allg. Chem.* **78**, 309 (1929).
18. Babb, S. E., *Rev. Mod. Phys.* **35**, 400 (1963).
19. Kennedy, G. C., private communication.