Solid-Liquid Equilibria under High Pressure of Nine Pure n-Alkylbenzenes

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The melting temperatures of nine *n*-alkylbenzenes (undecylbenzene, dodecylbenzene, tridecylbenzene, tetradecylbenzene, pentadecylbenzene, hexadecylbenzene, heptadecylbenzene, octadecylbenzene, and nonadecylbenzene) were measured by means of a high-pressure microscope up to 100 MPa. The experimental device used in this work allowed the distinction between stable and metastable solid phases. The influences of the alkyl chain length and pressure on the melting temperatures of the stable solid phases are discussed.

Introduction

During exploitation and transport of crude oils, solid particles may form because of high variations in temperature and pressure between reservoir and surface conditions. They cause an increase in the oil viscosity and, when they agglomerate and stick to the pipeline walls, a reduction in the effective cross section available for the flow. The pipes can even clog, triggering off a stoppage of the whole production line. These problems lead to important losses in production and high remediation or prevention costs.

As normal alkanes are mainly responsible for solid deposits, many works in the literature deal with their melting properties at atmospheric pressure $^{1-3}$ and under high pressure. However, other fractions of crude oils, such as naphthenes and aromatics, can alter the formation and the development of macrocrystalline wax obtained from solidification of n-alkanes. Recently, the lack of liquid—solid transition data for n-alkylcyclohexanes was pointed out, and eight compounds from this naphthenic family were studied. 10

Research on aromatics has mainly dealt with the liquid phase or transport properties of the lighter compounds. $^{11-15}$ For example, benzene and toluene are known to be good solvents for wax deposits 16 and have been studied in binary mixtures 6,17 and in more complex systems. 18 However on heavier compounds, particularly n-alkylbenzenes with more than 16 carbon atoms, recent research is very limited: Dorset 19 released the crystallographic structure of 1-phenyloctadecane and of 1-phenylnonadecane, which has also been mentioned by Sirota et al. 20 In the field of solid—liquid phase equilibria (SLE), Flöter et al. 21,22 have studied (P, T) diagrams of binary systems including 1-phenyldodecane. As for naphthenes, little data exist on SLE of heavy aromatics.

In this study, the melting temperatures of nine n-alkylbenzenes between 1-phenylundecane and 1-phenylundecane have been measured as a function of pressure in the (0.1 to 100) MPa range. Most of these compounds have already been studied at atmospheric pressure by several authors, $^{23-42}$ but a review of the related results has shown their inaccuracy or inconsistency. The aim of this study is to clarify those results by proposing

Table 1. List of the Studied Pure *n*-Alkylbenzenes

name	abbreviation	CASRN	mass fraction/%	origin
1-phenylundecane	phenylC ₁₁	6742-54-7	99.6	Aldrich
1-phenyldodecane	$phenylC_{12}$	123-01-3	99.7	Merck
1-phenyltridecane	phenylC ₁₃	123-02-4	99.5	TCI
1-phenyltetradecane	phenylC ₁₄	1459-10-5	98.6	Fluka
1-phenylpentadecane	phenylC ₁₅	2131-18-2	98.6	TCI
1-phenylhexadecane	phenylC ₁₆	1459-09-2	99.8	TCI
1-phenylheptadecane	phenylC ₁₇	14752-75-1	97.0	Fluka
1-phenyloctadecane	phenylC ₁₈	4445-07-2	97.0	Fluka
1-phenylnonadecane	phenylC ₁₉	29136-19-4	98.3	TCI

more reliable values. The influences of the number of carbon atoms and pressure on the melting temperatures will be discussed.

Experimental

Chemicals. The nine pure compounds studied in this work are 1-phenylundecane (or undecylbenzene), 1-phenyldodecane (or dodecylbenzene), 1-phenyltridecane (or tridecylbenzene), 1-phenyltetradecane (or tetradecylbenzene), 1-phenylpentadecane (or pentadecylbenzene), 1-phenylhexadecane (or hexadecylbenzene), 1-phenylheptadecane (or heptadecylbenzene), 1-phenyloctadecane (or octadecylbenzene), and 1-phenylnonadecane (or nonadecylbenzene). Their purities, CAS registry numbers, and origins are listed in Table 1. They were used without further purification. For practical purposes, their name will be abbreviated to phenylC $_n$, where n corresponds to the number of carbon atoms in the alkyl chain.

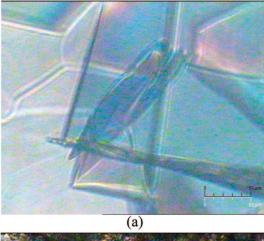
High-Pressure Microscopy Device. The experimental apparatus designed to work from (0.1 to 100) MPa in a temperature range of (243 to 373) K has been described in detail previously in Daridon et al.⁴³ The high-pressure microscope was built around an autoclave cell, made up of a stainless steel block and equipped with two sapphire windows through which the studied sample can be observed with the help of a polarizing microscope coupled with a video camera. Such a device allows the detection of 2 μ m diameter crystals.

The temperature of the whole cell was controlled by a heat-transducing fluid that circulates in four flow lines inside the metallic block. The thermal regulation of this fluid was carried out by a thermostat bath with a temperature stability of 0.01 K. The temperature of the sample was measured by means of a

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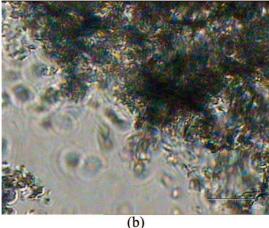


Figure 1. Snapshots of the two solid phases of the 1-phenyloctadecane: (a) metastable phase; (b) stable phase.

platinum resistance temperature detector inserted into a hole made in the cell. The accuracy of the temperature probe is 0.2 K.

The pressure was transmitted to the sample through a hand pump and measured with a flush diaphragm pressure transmitter, with a precision of 0.2 %.

Experimental Procedure. To properly measure a melting temperature, the system has to be at the thermodynamic equilibrium. To avoid metastable liquid phases due to subcooling effects, the measurements were performed on heating rather than on cooling. The sample was introduced in the cell in the liquid state after preheating the compounds that are solid at atmospheric pressure and ambient temperature. It was then cooled at constant pressure until crystallization.

In previous works, the study of solid-liquid equilibria of pure *n*-alkylcyclohexanes¹⁰ and of binary systems composed of normal alkanes⁴⁴ revealed the presence of metastable solid phases. This phenomenon, which can lead to highly underestimated melting temperatures if not adequately controlled, is common in compounds with long alkyl chains and was also observed for the n-alkylbenzenes under study. To induce the formation of the stable solid phase, the pressure of the system was temporarily increased at constant temperature and maintained at this value for a few seconds. If the first solid phase formed was metastable, this process forced it to quickly convert into a stable phase. This conversion can be easily monitored through the microscope as the stable and metastable phases do not have the same refractive indexes and appearance (Figure 1). The pressure was then lowered to its initial value, and the

Table 2. Melting Temperature $T_{\rm m}$ of the *n*-Alkylbenzenes as a Function of Pressure P

P/MPa	$T_{ m m}/{ m K}$	P/MPa	$T_{ m m}/{ m K}$	P/MPa	$T_{ m m}/{ m K}$	
phenylC ₁₁		pheny	phenylC ₁₂		phenylC ₁₃	
0.1	256.9	0.1	269.7	0.1	272.8	
20.6	261.4	20.2	274.4	20.1	277.3	
40.4	265.5	40.1	279.0	40.3	281.6	
60.9	269.7	60.0	283.4	60.8	285.9	
81.0	273.7	79.9	287.8	79.9	289.8	
99.9	277.1	100.0	292.0	100.1	293.7	
phen	ylC ₁₄	pheny	/lC ₁₅	pheny	/lC ₁₆	
0.1	289.1	0.1	285.1	0.1	299.5	
20.5	293.7	21.0	289.7	20.0	304.2	
40.0	297.8	40.1	294.1	40.3	308.6	
60.3	302.0	59.9	298.4	59.9	312.6	
80.4	306.0	80.4	302.8	80.4	316.8	
99.7	309.7	100.2	306.7	100.7	320.9	
phenylC ₁₇		phenylC ₁₈		phenylC ₁₉		
0.1	292.8	0.1	307.9	0.1	302.6	
		20.1	312.5	20.0	307.2	
		50.3	319.5	40.2	311.6	
		74.9	324.5	80.2	319.7	
		99.6	329.5	99.6	322.9	

Table 3. Deviations between the Melting Temperatures at Atmospheric Pressure Measured in this Work (T_m) and the Ones Found in the Literature (T_{ref})

	$T_{\rm ref}/{ m K}$	$T_{\rm m} - T_{\rm ref} / { m K}$		$T_{\rm ref}/{ m K}$	$T_{\rm m} - T_{\rm ref} / { m K}$
phenylC ₁₂	266^{23}	3.7	phenylC ₁₇	311^{32}	-11.5
	270^{24}	-0.3	phenylC ₁₈	302^{27}	5.9
	270.6^{21}	-0.9		303^{33}	4.9
phenylC ₁₄	282^{24}	7.1		306^{34}	1.9
	282.8^{25}	6.3		$308^{28,35}$	-0.1
phenylC ₁₆	280.0^{26}	19.5		309^{36-39}	-1.1
1 10	295^{27}	4.5		310^{40}	-2.1
	298^{28}	1.5	phenylC ₁₉	298.2^{41}	4.4
	$300^{29,30}$	-0.5		302.7^{42}	-0.1
	314^{31}	-14.5			

system was maintained in these experimental conditions for a few minutes until thermodynamic equilibrium was reached.

The sample was then heated stepwise with an increase of (0.1 or 0.2) K every (5 or 10) min depending on the proximity of the melting point. To minimize the effect of the impurities on the measured melting temperature, as these would melt before the pure compound, the measures were taken at the disappearance of the last crystal. The uncertainty on the melting temperature values is estimated at 0.2 K.

Results and Discussion

Melting Temperatures at Atmospheric Pressure. The melting temperature at atmospheric pressure of each compound, measured by means of the microscope technique described above, is reported in Table 2. These pure *n*-alkylbenzenes were difficult to crystallize, presenting a high degree of subcooling. Moreover, all compounds, except 1-phenylundecane, 1-phenyldodecane, and 1-phenyltridecane, presented a metastable solid phase during crystallization.

Table 3 presents the deviations between the melting temperatures measured in this study at atmospheric pressure and those previously reported in the literature. ^{21,23–42} No data have been found about 1-phenylundecane, 1-phenyltridecane, and 1-phenylpentadecane. A high disparity can be noticed among the different results for some compounds, e.g., a gap greater than 30 K between the extreme melting temperatures reported for 1-phenylhexadecane. There are two explanations for this phenomenon. First, some results are quite dated, and in the past, solid-liquid transitions were often measured on cooling rather

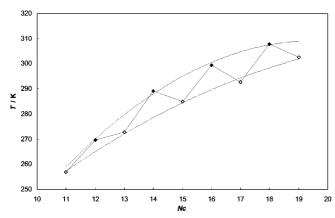


Figure 2. Melting temperature $T_{\rm m}$ of the *n*-alkylbenzenes as a function of the number of carbon atoms $N_{\rm C}$ present in the alkyl chain: \blacklozenge , even $N_{\rm C}$; \diamondsuit ,

Table 4. Deviation between the Melting Temperatures T_{ref} of 1-Phenyldodecane Released by Flöter et al. 21 and Our Interpolated Data (T_m) for Various Pressures

P/MPa	$T_{\rm ref}/{ m K}$	$T_{\rm m}-T_{\rm ref}/{ m K}$
31.08	276.95	0.02
44.23	279.95	-0.05
58.08	282.95	0.00
80.66	287.95	-0.09

than on heating, involving an underestimation of the melting temperatures particularly for compounds like *n*-alkylbenzenes for which subcooling is important. Second, as mentioned above, almost all studied compounds present a metastable solid phase, the melting temperature of which is lower than the one of the stable phase. If the sample is heated immediately after the metastable crystals have appeared, those crystals melt and return to the undercooled liquid state, giving the impression of a normal transition point. As these metastable solid phases have a relatively high stability, it is necessary to lower the temperature of the studied system or to increase the pressure temporarily to make the stable phase appear. This procedure should always be applied to check if the crystals are from stable phases or not, but some experimental devices do not allow one to do so. Therefore, some melting temperatures available in the literature are erroneous due to at least one of the problems mentioned above. For example, the melting temperatures given for the 1-phenyltetradecane [(282 and 282.8) K]^{24,25} are coherent; however, they correspond in fact to the melting point of the metastable phase we measured at 282.6 K, whereas the stable phase disappears at 289.1 K. In the case of the 1-phenylnonadecane, the value reported by Meyer and Meyer 42 (302.7 K) is in very good agreement with ours (302.6 K). But Chu et al.41 have presented a melting temperature for this compound at 298.2 K, which corresponds in fact to the melting point of the metastable phase we measured at this same temperature. Meyer and Meyer⁴² also mentioned this melting point at 298.1 K.

Figure 2 shows the variation of the melting temperature of the *n*-alkylbenzenes as a function of the length of the alkyl chain. Usually for the hydrocarbons, the longer the alkyl chain, the higher the melting temperature, although a more or less pronounced parity effect is observed. 10,45 Here, the parity effect is so important that the addition of a -CH2- group does not necessarily lead to an increase in the melting temperature unlike for *n*-alkanes⁴⁵ or *n*-alkylcyclohexanes.¹⁰ However, for compounds with the same parity, the usual rule remains true.

Melting Temperatures under High Pressure. The melting temperature of each n-alkylbenzene has been measured as a

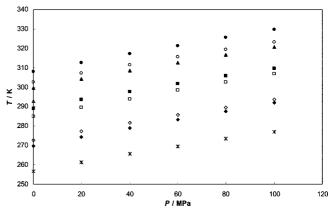


Figure 3. Melting temperature $T_{\rm m}$ of the *n*-alkylbenzenes as a function of pressure P: *, phenyl C_{11} ; \blacklozenge , phenyl C_{12} ; \diamondsuit , phenyl C_{13} ; \blacksquare , phenyl C_{14} ; \Box , phenyl C_{15} ; \blacktriangle , phenyl C_{16} ; \triangle , phenyl C_{17} ; \blacksquare , phenyl C_{18} ; \bigcirc , phenyl C_{19} .

Table 5. Average Slope $\Delta T/\Delta P$ of the Solid-Liquid Transition **Curve for Each Compound**

	average slope/K⋅MPa ⁻¹
phenylC ₁₁	0.202 ± 0.004
phenylC ₁₂	0.224 ± 0.004
phenylC ₁₃	0.209 ± 0.004
phenylC ₁₄	0.207 ± 0.004
phenylC ₁₅	0.216 ± 0.004
phenylC ₁₆	0.212 ± 0.004
phenylC ₁₈	0.217 ± 0.004
phenylC ₁₉	0.205 ± 0.004

function of pressure in the (0.1 to 100) MPa range. The results are listed in Table 2. Only the melting temperature at atmospheric pressure is available for 1-phenylheptadecane due to experimental failure.

A comparison of the melting temperatures measured for the *n*-phenyldodecane with those proposed by Flöter et al.²¹ with a reported uncertainty of 0.25 K is presented in Table 4. It shows that the deviation between their measurements and our interpolated values is in average of 0.04 K with a maximum deviation of -0.09 K. These values are inferior to the accuracy of the temperature probe, which confirms the quality of the measurements presented here.

The liquid-solid transition curves in the (T, P) diagram are represented in Figure 3. They reveal a quasilinear relationship between melting temperature and pressure. This dependence has been quantified by calculating the average slope of each curve (cf. Table 5) as follows:

$$\frac{\Delta T}{\Delta P} = \frac{T_{\rm m}(P_{\rm max}) - T_{\rm m}(P_{\rm atm})}{P_{\rm max} - P_{\rm atm}} \tag{1}$$

where $P_{\rm atm}$ is the atmospheric pressure and $P_{\rm max}$ is the maximum pressure available for each compound (≈100 MPa). Thus, the uncertainty on the value of the average slope has been estimated at 2 %.

In previous studies dealing with liquid—solid equilibria of n-alkane binary systems⁴⁵ or with the melting temperatures of *n*-alkylcyclohexanes, ¹⁰ it appeared that the crystalline structure of the melting solid phase and then the parity of the compounds had an influence on the slopes of the transition curves. In the case of *n*-alkylbenzenes, Figure 4 shows that conclusion to be less evident. By looking at the results of 1-phenylundecane, 1-phenyltridecane and 1-phenylpentadecane for the odd compounds and those of 1-phenyltetradecane, 1-phenylhexadecane and 1-phenyloctadecane for the even ones, it seems that the slope of the transition curve increases with the length of the

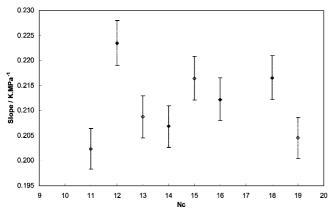


Figure 4. Average slope of the solid—liquid transition curves as a function of the number of carbon atoms $N_{\rm C}$ present in the alkyl chain: \blacklozenge , even $N_{\rm C}$; \diamondsuit , odd $N_{\rm C}$.

alkyl chain, with a strong parity effect that should reveal different crystalline structures for odd and even compounds. However, the results concerning 1-phenyldodecane and 1-phenylnonadecane do not match these trends and may be explained by the presence of additional crystalline structures in this family.

Conclusion

A literature review revealed an important lack of reliable data concerning solid-liquid transition of aromatics, particularly *n*-alkylbenzenes. In this study, the melting temperatures of nine n-alkylbenzenes have been measured by means of a highpressure microscope in the (0.1 to 100) MPa range. The study at atmospheric pressure pointed out the difficulties of such measurements due to the appearance of metastable solid phases during crystallization for almost all compounds. The experimental device used in this work avoids such issues thanks to the use of the pressurizing pump which makes it easier for the stable crystals to form. Besides, the metastable-stable transition can be easily checked by the help of visual monitoring. The melting temperatures of the studied n-alkylbenzenes have revealed to be strongly dependent on the parity of the number of carbon atoms. This parity effect is more important than the one observed for normal alkanes or even for n-alkylcyclohexanes.

Eventually, the melting temperatures showed a quasilinear dependence on pressure. The average slopes of the solid—liquid transition curves in a (T, P) diagram have also been discussed and reveal different crystalline structures for odd and even compounds.

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