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Solid−Liquid Equilibria under High Pressure of Eight Pure *n*-Alkylcyclohexanes

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The melting temperature of eight *n*-alkylcyclohexanes (decylcyclohexane, undecylcyclohexane, dodecylcyclohexane, tridecylcyclohexane, tetradecylcyclohexane, pentadecylcyclohexane, octadecylcyclohexane, and nonadecylcyclohexane) has been measured by means of a high-pressure microscopy device up to 100 MPa. The influence of the alkyl chain length on the melting temperatures and their pressure dependence is discussed.

Introduction

The formation of solid deposits in crude oils is a major issue in the petroleum industry because it is responsible for important losses in production and high remediation or prevention costs. These fluids are indeed subject to high variations in pressure and temperature during their exploitation and transportation, such that hydrocarbons of high molecular weight can precipitate, leading to higher pumping costs due to an increase in the oil viscosity and an effective reduction in the cross section of the pipelines. In the worst case, the crystals can agglomerate and block the pipes, triggering off a stoppage of the whole production line.[1]

Several works in the literature have already studied the solid−liquid equilibria (SLE) of paraffinic systems like synthetic mixtures,[2−6] fuels,[7−9] and degassed oils.[10−16] Modeling of such equilibria requires precise information about the pure compounds thermophysical properties and in particular their melting temperatures. As normal alkanes are mainly responsible for solid deposits, a lot of data about their melting properties at atmospheric pressure[17−19] and under high pressure[20−24] can be found in the literature. However crude oils contain many other component families such as naphthenes that may also be present in solid deposits formed in pipelines.[25] Naphthenes are often found as microcrystalline wax in reservoir mud,[1] but they can also be present in macrocrystalline wax (obtained from solidification of *n*-alkanes)[26,27] of which development can be altered due to the presence of these cyclic alkanes.[1] According to Hammami and Raines,[28] those naphthenes can disturb and even interrupt the nucleation process or the crystal growth of paraffins.

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

name	abbreviation	CASRN	mass fraction/%
decylcyclohexane	cycloC_6C_{10}	1795-16-0	99.7
undecylcyclohexane	cycloC_6C_{11}	54105-66-7	99.3
dodecylcyclohexane	cycloC_6C_{12}	1795-17-1	99.7
tridecylcyclohexane	cycloC_6C_{13}	6006-33-3	99.0
tetradecylcyclohexane	cycloC_6C_{14}	1795-18-2	99.2
pentadecylcyclohexane	cycloC_6C_{15}	6006-95-7	99.0
octadecylcyclohexane	cycloC_6C_{18}	4445-06-1	99.0
nonadecylcyclohexane	cycloC_6C_{19}	22349-03-7	99.5

Despite their role in the formation of solid deposits, SLE of naphthenes under high pressure remain much less studied than those of normal alkanes. Since the 1940s, several authors have measured the melting temperature of naphthenes at atmospheric pressure[29−36] or their crystal−liquid−gas triple points.[37] On recent works, binary systems composed of cyclohexane and normal paraffins have been studied at atmospheric pressure[38] or under high pressure,[20,22] but very limited data for naphthenes of high molecular weight are available. Sirota et al.[39] have investigated the phase behavior of the nonadecylcyclohexane at atmospheric pressure with the help of crystallographic, calorimetric (DSC), and microscopic measurements. Dorset[40] has also underlined the crystalline structure of this compound, while Cordoba and Schall[25] have observed its behavior in a solvent in flow conditions. Young and Schall[27] have studied the solubility of the pentadecylcyclohexane and nonadecylcyclohexane in various solvents, and they have suggested a phase diagram of the binary systems {pentadecylcyclohexane + nonadecylcyclohexane} and {octadecylcyclohexane + nonadecylcyclohexane}.[41] Consequently, except for nonadecylcyclohexane, which has been studied by several authors, the SLE of naphthenes of high molecular weight have been understudied, particularly under high pressure.

In this work, the melting temperature of eight pure *n*-alkylcyclohexanes with at least 16 carbon atoms has been measured in the (0.1 to 100) MPa pressure range, by means of a high-pressure microscopy device. The slopes of the solid−liquid transition curves in a (T, P) diagram (i.e., the pressure dependence of the melting temperatures) will be discussed.

Experimental Section

Chemicals. The eight pure compounds studied in this work are decylcyclohexane, undecylcyclohexane, dodecylcyclohexane, tridecylcyclohexane, tetradecylcyclohexane, pentadecylcyclohexane, octadecylcyclohexane, and nonadecylcyclohexane. Their purities and their CAS registry numbers (CASRN) are listed in Table 1. They were purchased from Tokyo Chemical Industry and were used without further purification. For practical reasons, their name will be abbreviated as cycloC_6C_n, where n corresponds to the number of carbon atoms in the alkyl chain.

High-Pressure Microscopy Device. The experimental apparatus used in order to measure the melting temperature of the *n*-alkylcyclohexanes and designed to work from (0.1 to 100) MPa in a temperature range of (243 to 373) K has already been described in detail in a previous paper.[42] The high-pressure

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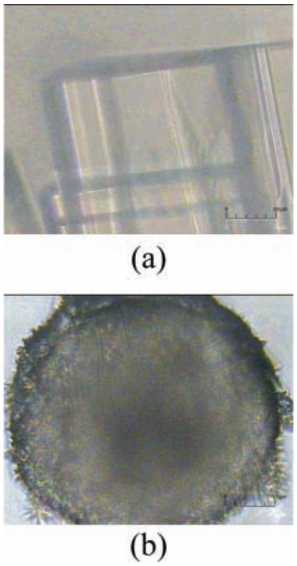

(a)

(b)

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

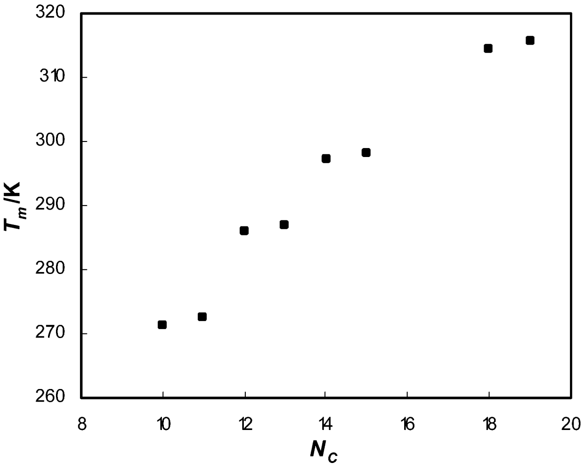

Figure 2. Melting temperature T_m of the *n*-alkylcyclohexanes as a function of the number of carbon atoms N_C present in the alkyl chain.

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 crystals with 2 μm in diameter.

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 platinum resistance temperature detector inserted into a hole made in the cell. The uncertainty of temperature values is estimated to be 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 %.

Procedures. 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. Then it was cooled at constant pressure until its crystallization.

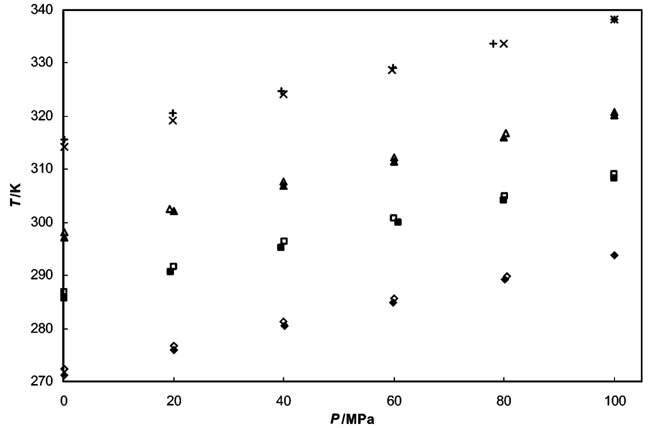

Figure 3. Melting temperature T_m of the *n*-alkylcyclohexanes as a function of pressure *P*: ◆, cycloC_6C_{10}; ◇, cycloC_6C_{11}; ■, cycloC_6C_{12}; □, cycloC_6C_{13}; ▲, cycloC_6C_{14}; △, cycloC_6C_{15}; ×, cycloC_6C_{18}; +, cycloC_6C_{19}.

In a previous work,[43] the study of solid−liquid equilibria of binary systems composed of normal alkanes revealed the presence of metastable solid phases. This phenomenon is common in compounds with long alkyl chains and may also occur for the *n*-alkylcyclohexanes 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 to form was metastable, this process helped that it quickly converts into a stable phase. This conversion can be easily monitored thanks to the microscope as the stable and metastable phases have not the same appearance (Figure 1). The pressure was then lowered to its initial value, and the 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. In order to minimize the effect of the impurities on the measured melting temperature, as these would melt before the pure compound, the measurement was done at the temperature when the last crystal disappeared. 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 described above, is reported in Table 2. These pure compounds were difficult to crystallize, presenting high degree of subcooling, and it was necessary to decrease the temperature around 10 K below their melting temperature or to increase the pressure by approximately 50 MPa, in order to make the crystals appear. No metastable solid phase was detected, except for the nonadecylcyclohexane, which will be discussed below.

Table 3 presents the deviations between the melting temperatures measured in this work at atmospheric pressure and data previously reported in the literature.[27,29−36,39,44] Some large deviations found can be explained by the poor quality of the reference data. For example, the melting temperatures reported by Shakarashvili and Bekauri[35] or by Larsen et al.[32] with deviations to our data of (3.5 and 2.1) K, respectively, present an uncertainty of 2 K according to the Thermodynamics Research Center.[45] If the data of lower quality are not taken into account, the average absolute deviation is equal to the precision of the temperature probe (0.2 K), which shows a good agreement between the melting temperatures obtained by the microscopy device and the literature data.

Table 2. Melting Temperature T_m of the *n*-Alkylcyclohexanes as a Function of Pressure P[a]

cycloC_6C_{10}		cycloC_6C_{11}		cycloC_6C_{12}		cycloC_6C_{13}		cycloC_6C_{14}		cycloC_6C_{15}		cycloC_6C_{18}		cycloC_6C_{19}	
P/MPa	T_m/K	P/MPa	T_m/K	P/MPa	T_m/K	P/MPa	T_m/K	P/MPa	T_m/K	P/MPa	T_m/K	P/MPa	T_m/K	P/MPa	T_m/K
0.1	271.3	0.1	272.4	0.1	285.8	0.1	286.9	0.1	297.2	0.1	298.1	0.1	314.3	0.1	315.7
20.0	276.0	20.0	276.8	19.5	290.6	20.0	291.7	20.0	302.2	19.3	302.6	20.0	319.3	19.8	320.6
40.1	280.5	40.0	281.3	39.6	295.2	40.2	296.3	39.9	307.0	40.0	307.6	39.9	324.2	39.5	324.8
59.9	284.8	60.0	285.7	60.9	299.9	60.0	300.7	60.0	311.5	60.1	312.3	59.6	328.8	59.8	329.2
80.1	289.2	80.5	289.9	79.9	304.2	80.1	304.9	79.9	316.0	80.3	316.8	80.0	333.6*	78.0	333.7
100.1	293.9	100.0	293.9	100.0	308.4	100.0	309.1	100.1	320.3	100.1	320.8	100.0	338.3*	100.0	338.3*

[a] The values followed by an asterisk have been extrapolated.

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

	T_{ref}/K	$T_m - T_{ref}$/K
cycloC_6C_{10}	271.1[30]	0.2
	271.4[36]	-0.1
cycloC_6C_{12}	282[35]	3.5
	285[34]	0.8
cycloC_6C_{14}	298[34]	−0.8
cycloC_6C_{15}	298.2[27]	−0.1
cycloC_6C_{18}	314[31]	0.1
	314.7[33]	−0.4
	314.8[29]	−0.5
	316[32]	−2.1
cycloC_6C_{19}	315.7[27,44]	0.0
	316.2[39]	−0.5

Figure 2 shows the variation of the melting temperature of the *n*-alkylcyclohexanes as a function of the length of the alkyl chain. It reveals that the addition of a -CH_2- group leads to an increase in the melting temperature with an important parity effect, stronger than for normal alkanes.[46]

As previously mentioned, the behavior of nonadecylcyclohexane differs from the other compounds because it presents a metastable solid phase. Sirota et al.[39] have studied the appearance conditions of this phase at atmospheric pressure and the kinetics of conversion to the stable phase. When the temperature decreases, the sample first crystallizes in the metastable phase (Figure 1). If the cooling rate is too high ($\geq$ 10 K·min^{-1}), the temperature falls too fast to allow crystalline restructuring and the sample remains in metastable phase. Otherwise, the stable phase always appears (Figure 2) but the conversion metastable → stable is complete only when the cooling rate is below 5 K·min^{-1}. It is worth underlining that the conversion between both solid phases is very slow: according to Sirota et al.,[39] the conversion time is the shortest around 288 K, but it is all the same in the order of a few minutes.

It is possible to exploit this relative stability of the metastable solid phase to measure its melting temperature. In fact, if the stable solid phase has not appeared, an increase in temperature just after crystallization makes the metastable solid-phase melt and the sample returns to an under-cooled liquid state. The measured melting temperature of the metastable phase at atmospheric pressure is 302.7 K, in good agreement with the values (302.8 and 303.1) K reported respectively by Sirota et al.[39] and Meyer and Meyer.[44] Interestingly, the melting temperature of the stable solid phase (315.7 K) is 13 K higher than that of the metastable phase. This 13 K range actually corresponds to the undercooling area in the phase diagram of nonadecylcyclohexane. Therefore, in a cooling process, no crystallization can occur while the temperature of the sample, initially at liquid state, is greater than the melting temperature of the metastable phase. Below 302.7 K, the metastable solid phase appears, followed by the stable phase if the experimental conditions are favorable as discussed above.

Table 4. Average Slope $\Delta T/\Delta P$ of the Liquidus Curves for Each Compound

	average slope/K·MPa^{-1}
cycloC_6C_{10}	0.226 ± 0.005
cycloC_6C_{11}	0.215 ± 0.004
cycloC_6C_{12}	0.226 ± 0.005
cycloC_6C_{13}	0.223 ± 0.004
cycloC_6C_{14}	0.231 ± 0.005
cycloC_6C_{15}	0.227 ± 0.005
cycloC_6C_{18}	0.240 ± 0.005
cycloC_6C_{19}	0.226 ± 0.005

Melting Temperatures under High Pressure. The melting temperature of each *n*-alkylcyclohexane has been measured as a function of pressure in the (0.1 to 100) MPa range. The results are listed in Table 2. Some measurements could not be performed due to experimental failure for the octadecylcyclohexane or because of the temperature limitations we fixed for the nonadecylcyclohexane. In these cases, the melting temperatures have been estimated by means of a polynomial extrapolation in order to compare the slopes of the liquidus curves in the whole pressure range.

The liquidus curves in the (T, P) diagram are represented in Figure 3. They reveal a quasi-linear relationship between melting temperature and pressure. This dependence has been quantified by calculating the average slope of each curve (cf. Table 4) as follows:

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

where P_{atm} is the atmospheric pressure and P_{max} the maximum pressure available for each compound ($\approx$ 100 MPa). Thus, the uncertainty on the value of the average slope has been estimated at 2 %. For the octadecylcyclohexane and nonadecylcyclohexane, the extrapolated melting temperatures have been used because the average slopes calculated with other data would be overestimated due to the slight concavity of the curves. Figure 4 shows the variation of the average slope as a function of the length of the alkyl chain: *n*-alkylcyclohexanes with an even number of carbon atoms present an average slope greater than their odd homologue, but for two compounds with same parity, the slope increases with the length of the alkyl chain. As shown in a previous work dealing with the solid−liquid equilibria of *n*-alkanes, the average slope of a liquidus curve depends on the crystalline structure of the melting solid phase. Therefore, it seems that even and odd *n*-alkylcyclohexanes have different crystalline states.

In order to complete this study, the melting temperature of the nonadecylcyclohexane's metastable phase as a function of pressure is reported in Table 5. It has not been possible to perform measurements at (80 and 100) MPa because the higher the pressure the faster the stable phase appears. However, the data have been extrapolated for comparative purpose (cf. Figure 5). The average slope of the metastable liquidus curve is equal

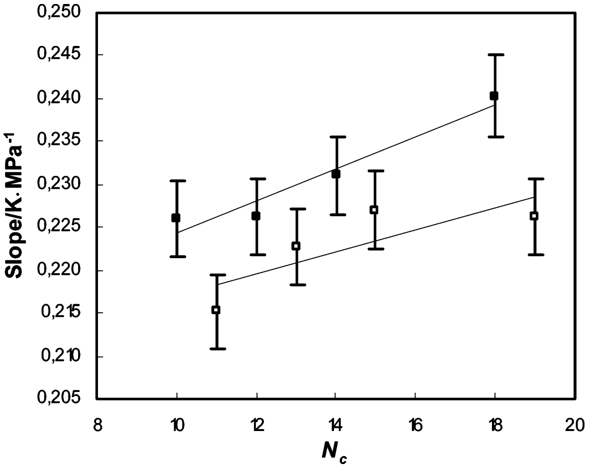

Figure 4. Average slope of the liquidus curves as a function of the number of carbon atoms N_C present in the alkyl chain: ■, even N_C; □, odd N_C.

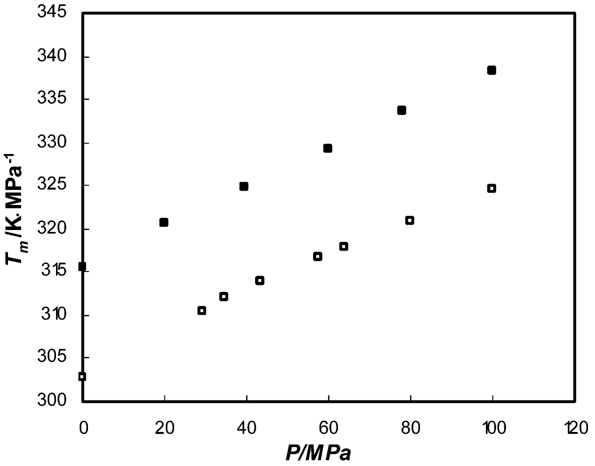

Figure 5. Melting temperature T_m of the nonadecylcyclohexane as a function of pressure P: ■, stable solid phase; □, metastable solid phase.

Table 5. Melting Temperature T_m of the Nonadecylcyclohexane's Metastable Phase as a Function of Pressure P^a

P/MPa	T_m/K	P/MPa	T_m/K
0.1	302.8	57.8	316.6
29.5	310.5	64.0	317.9
34.4	312.1	80.0	320.9*
43.2	313.9	100.0	324.6*

^{a} The values followed by an asterisk have been extrapolated.

to (0.219 ± 0.004) K·MPa^{-1}, which is close to the one of the stable phase (0.226 ± 0.005) K·MPa^{-1}. Therefore, it is not possible to differentiate the two solid phases only by the study of the melting temperature as a function of pressure, as was done before for the *n*-alkanes.[43] Nevertheless, the required extrapolation could have introduced some extra uncertainties that obstruct more directly meaningful results.

Conclusions

There is an important lack of data concerning the melting temperatures of naphthenes. In this work, the solid−liquid equilibria of eight *n*-alkylcyclohexanes have been investigated by means of a high-pressure microscopy device in the (0.1 to 100) MPa range. The study at atmospheric pressure has revealed a good agreement between the melting temperatures measured in this work and the data available in the literature, including the case of the metastable solid phase of the nonadecylcyclohexane. The melting temperatures of these compounds strongly depend on the parity of the number of carbon atoms present in the alkyl chain. This parity effect is more important than the one observed for normal alkanes. Finally, the melting temperatures show a quasi-linear dependence on the pressure. The average slope of the liquidus curves in a (T, P) diagram is also dependent on the parity of the alkyl chain.

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