



Experimental thermophysical properties of n-alkanes from C17 to C50 and validation of available correlations

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Abstract

Wax precipitation inside the pipelines can partially block the oil flow and create serious safety and financial issues in the oil and gas industry. Reliable experimental values for thermophysical properties on n-alkanes are required as input to accurately predict precipitation and then deposition behavior. Several correlations have been proposed based on limited experimental data reported in different settings over several decades ago. This work aims to conduct experiments to collect thermophysical properties for pure n-alkanes with carbon numbers ranging from 17 to 50 using a micro differential scanning calorimeter and validate the available correlations.

Keywords

Thermodynamic properties; paraffin wax; thermodynamic modeling

Introduction

The term flow assurance refers to a set of strategies and principles that assure oil production without interruption [1]. The complexity of the multiphase flow combined with hostile environments of the pipeline systems in ultradeep waters has increased the importance of this discipline. Along with asphaltene and hydrate deposition, wax precipitation and deposition are severe economic and safety concerns for the oil and gas industry.

During oil production, the fluid temperature varies because of the heat exchange with the surrounding environment. As the oil temperature reaches the wax appearance temperature (WAT), the liquid phase will be saturated with solid particles (phase transition) dissolved. As the oil temperature decreases, the wax particles may precipitate and transport to the pipe wall and deposit [2]. Since phase transition is a thermodynamic phenomenon, it is essential to describe the wax precipitation accurately.

Won (1986) [3] stated that the solid phase is composed of a single and homogeneous solid solution in equilibrium with the liquid phase. Lira-Galeana et al. (1996) [4] introduced the multi-solid theory in which multiple phases form the solid phase. In this case, each solid phase is formed by pure n-alkane, and the solid phases are immiscible and independent. Later, Coutinho (1998) [5] introduced a theory affirming that the solid phase comprises multiple solid solutions. The accuracy of all these thermodynamic models depends heavily on the pure component thermophysical properties: temperature and enthalpy of fusion (T_f and H_f) and temperature and enthalpy of solid-solid transition

(T_{tr} and H_{tr}). Reliable experimental values for thermophysical properties are required as input data for the precipitation models since it directly impacts the accuracy of these models.

Finke et al. (1954) [6] measured the thermophysical properties of n-alkanes with carbon numbers ranging from 8 to 16 by using a calorimeter. Details of the experimental apparatus are given in Ruehrwein & Huffman (1943) [7]. Schaerer et al. (1955) [8] reported the thermophysical properties of n-alkanes with carbon numbers ranging from 17 to 30. The authors measured the thermophysical properties using an adiabatic calorimeter with electrical heating with an accuracy of $\pm 2\%$. Broadhurst (1962) [9] published a set of experimental data selected from the literature by considering the impurity of the n-alkanes and their consistency with data previously reported in the literature. Himram et al. (1994) [10] compiled data of T_f and H_f for n-alkanes with carbon numbers ranging from 1 to 100 that were reported in the literature. Over the years, several correlations have been proposed to estimate the thermophysical properties of the pure n-alkanes. For example, Coutinho (2000) [11] proposed correlations to estimate the thermophysical properties (T_f , H_f , T_{tr} , and H_{tr}) depending on the carbon chain size. Chen et al. (2007) [12] proposed correlations depending on the n-alkane with either odd or even carbon number and the carbon chain size. More simplistic correlations were also proposed by Won (1986) [3] as a function of the molecular weight.

All the data collected and reported by Broadhurst (1962) [9] and Himram et al. (1994) [10], are obtained from many different sources. Thus, it is important to have a set of experimental data with a

broader range of carbon numbers measured by the same apparatus at similar experimental conditions. Additionally, with the advancements in thermodynamic measurements techniques over the years, it would be useful to validate the existing correlations against an independent set of data measured by modern instruments. This work aims to conduct experiments to collect thermophysical properties for pure n-alkanes and validate the available correlations in the literature.

Methodology

A Setaram high-pressure micro differential scanning calorimeter (μ DSC-evo VII) was used to measure the thermophysical properties of the pure n-alkanes. The software CALISTO 2.02 acquisition and processing were used to obtain and process the data. The μ DSC is connected to a chiller to assist in controlling and maintaining the desired temperature; a schematic of the equipment was published in previous work [13].

After each experiment, all the thermograms were analyzed to obtain the fusion temperature, enthalpy and solid-solid transition temperature, and enthalpy for each pure n-paraffin. A build-in peaks separation procedure was used to obtain the precise latent heat and onset temperature values for each peak if the peaks overlap. The peaks separation procedure uses position, amplitude, half-width, and asymmetry to optimize the two peaks utilizing the application of Gaussian.

The percentage relative error (PRE), between the predicted values using correlations from the literature and experimental data obtained in this work, was calculated using Eq. 1. Then, the mean percentage relative error (MPRE) was calculated for each correlation.

$$PRE (\%) = \left| \frac{\alpha_{predicted} - \alpha_{experimental}}{\alpha_{experimental}} \right| \times 100 \quad (1)$$

Experimental Procedure

A total of 10 mg of the solid pure n-alkane was added to the test cell of the μ DSC. The sample is cooled to reach 15 degrees below its melting point at a rate of 2.0 K per minute. The sample is then heated at a rate of 0.2 K per minute to 15 degrees above its melting point and then held at a constant temperature for 3 minutes before cooling at a rate of 0.2 K per minute to 15 degrees below its melting point and holding at a constant temperature for an additional 3 minutes. During the cooling cycle, exothermic peaks were observed, indicating the formation of a solid and/or solid-solid transition phase. Endothermic peaks were observed during the heating cycle, indicating the melting of the pure n-alkane and a solid and/or solid-solid transition phase, as shown in Figure 1. This process was repeated three times to ensure data consistency. The results were analyzed to obtain the heat of dissociation, the area under each peak, and the onset temperatures, the point where the initial slope of the peak intersects with the baseline.

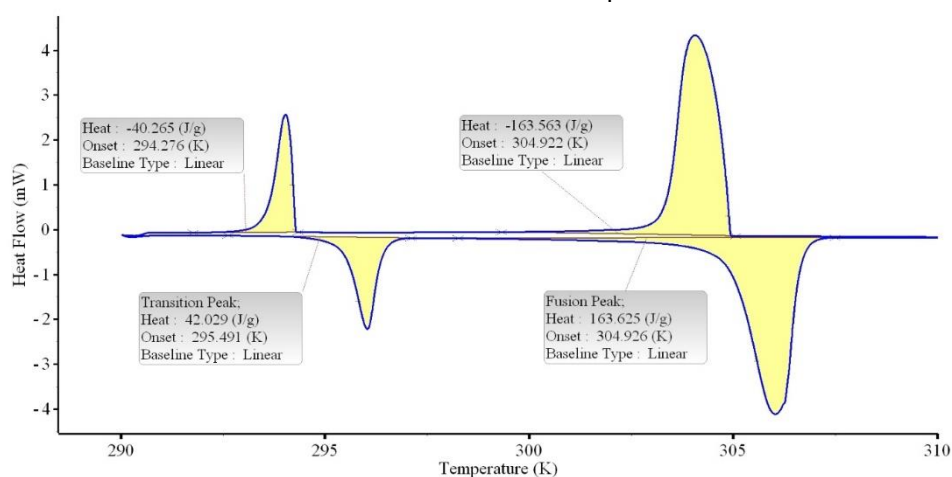


Figure 1: Sample thermogram of the pure n-alkanes nC19 to illustrate the operating procedure and the data analysis.

Results and Discussion

The experimental temperature of fusion measured (C17-C50) is consistent with the available literature (C17-C30) as can be seen in Figure 2. The figure also compares the available correlations with the experimental values. One could see that a simple correlation in carbon number or molecular weight can predict the temperature of fusion with great accuracy regardless of the carbon chain size or if it

is odd or even. This could be further illustrated where Won's correlation is a single correlation that is a function in molecular weight only while Ji et al. have a set of five correlations depending on the carbon chain size and if it is odd or even. Both showed an acceptable accuracy when compared to experimental values.

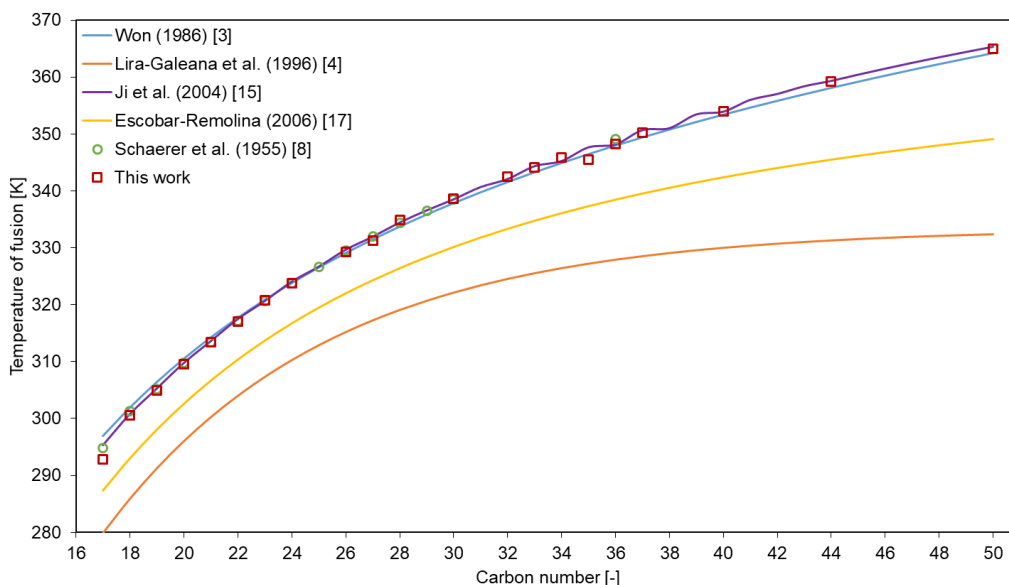


Figure 2: Experimental temperature of fusion vs. literature experimental values and some of the available correlations.

In order to quantify the correlations deviation from the experimental values and proposed the ones that are simple with accurate prediction, PREs and MPREs between the predicted values using correlations and experimental data for the temperature of fusion were given in Table 1. Five

correlations showed MPRE that is less than 0.5%. these correlations are Won (1986) [3], Coutinho (2000) [11], Coutinho and Daridon (2001) [14], Ji et al. (2004) [15], and Chen et al. (2007) [12]. Both Ji et al. (2004) [15] and Chen et al. (2007) [12] proposed a set of correlations rather than a single

Table 1: PREs between the predicted values using correlations from the literature and experimental data given in this work for T_f and MPRE of each correlation.

Carbon number	Exp.(K)	PRE (%)							
		[3]	[16]	[4]	[11]	[14]	[15]	[17]	[12]
17	292.85	1.39	2.64	4.46	0.86	0.82	0.83	1.91	1.39
18	300.59	0.43	3.17	4.90	0.08	0.04	0.05	2.55	0.43
19	304.87	0.50	2.79	4.47	0.04	0.11	0.13	2.26	0.50
20	309.56	0.30	2.73	4.38	0.08	0.01	0.06	2.27	0.30
21	313.45	0.25	2.58	4.22	0.03	0.02	0.04	2.18	0.25
22	317.00	0.22	2.45	4.11	0.03	0.05	0.15	2.11	0.22
23	320.73	0.04	2.49	4.18	0.04	0.05	0.03	2.21	0.04
24	323.75	0.02	2.41	4.16	0.02	0.02	0.09	2.19	0.02
26	329.20	0.03	2.33	4.25	0.12	0.05	0.14	2.21	0.03
27	331.30	0.06	2.21	4.23	0.26	0.19	0.20	2.13	0.06
28	334.84	0.33	2.57	4.70	0.08	0.16	0.12	2.53	0.33
30	338.56	0.21	2.45	4.84	0.09	0.04	0.01	2.50	0.21
32	342.42	0.25	2.54	5.21	0.06	0.06	0.10	2.67	0.25
33	344.14	0.25	2.58	5.39	0.07	0.08	0.06	2.74	0.66
34	345.79	0.25	2.63	5.59	0.07	0.10	0.16	2.82	0.55
35	345.53	0.28	2.16	5.29	0.60	0.65	0.62	2.39	0.09
36	348.28	0.09	2.57	5.83	0.25	0.30	0.03	2.83	0.18
37	350.27	0.24	2.79	6.19	0.11	0.15	0.12	3.08	0.26
40	353.99	0.16	2.94	6.76	0.32	0.24	0.02	3.29	0.00
44	359.22	0.30	3.43	7.76	0.68	0.09	0.04	3.83	0.01
50	364.89	0.18	3.94	8.90	2.73	0.11	0.12	4.34	0.15
MPRE (%)		0.28	2.69	5.23	0.31	0.16	0.15	2.62	0.28

one which adds a certain degree of unnecessary complexity. Coutinho (2000) [11] shows some deviation toward the higher end of the carbon range, namely C44 and C50, thus its usage is discouraged with heavier oils. Since neither Won (1986) [3] nor Coutinho and Daridon (2001) [14] did not set a range of applicability for their correlation, this work suggests won's correlation correlations to predict T_f for pure n-alkanes, because of their simplicity.

Other thermodynamic parameter analysis is in progress.

Conclusions

The temperature and enthalpy of fusion and solid-solid transition for n-alkanes were measured using a micro differential scanning calorimetry. In this section, only temperature of fusion was analyzed against literature experimental values and available correlations. It was found that several correlations will predict it with good accuracy. However, only two correlations were proposed by this work due to their simplicity have good precision. This work should clear an area of uncertainty in paraffin wax precipitation and deposition prediction since using the accurate thermophysical properties correlations is the initial step in paraffin wax modeling. Thus, the focus on increasing the accuracy of wax precipitation models should shift to other assumptions rather than input values.

Responsibility Notice

The authors are the only ones responsible for the paper content.

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