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Critical temperatures and pressures of C_{40}, C_{44}, and C_{60} normal alkanes measured by the pulse-heating technique

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ABSTRACT

The critical pressures and the critical temperatures of normal alkanes C_nH_{2n+2} with carbon numbers 40, 44, and 60 have been measured by the pulse-heating technique. A new method of calculation of the correction factors in pulse-heating experiments has been suggested. The results of earlier experiments (E.D. Nikitin, P.A. Pavlov, A.P. Popov, Fluid Phase Equilib., 141, 1997, pp. 155–164.) for n-alkanes with $n = 19$, 20, 21, 22, 23, 24, 26, 28, 30, and 36 have been recalculated using this method. Equations for the estimation of the critical temperatures and pressures of normal alkanes ($n \geq 5$) have been suggested. The experimental critical properties have been compared with the estimations made by the Constantinou/Gani method and equations developed by Lemmon and Goodwin.

1. Introduction

Project 851 of the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers has sponsored this study to measure the critical properties of the following heavy n-alkanes: n-tetracontane (CASRN 4181-95-7), n-tetratetracontane (CASRN 7098-22-8), n-hexacontane (CASRN 7667-80-3). The measurements were performed in 2009. Normal alkanes C_nH_{2n+2} are known to decompose at temperatures above approximately 650 K so n-alkanes from methane to decane are stable at the critical point and their critical properties have been investigated well enough [1]. However, all the n-alkanes heavier than decane are unstable and as the carbon number increases they become progressively more unstable; it makes measuring the critical constants of these alkanes a complex problem. The critical properties of n-alkanes from undecane ($n = 11$) to octadecane ($n = 18$) have been measured by Ambrose et al. [2–4], Teja et al. [5–7], Pak and Kay [8], Matzik and Schneider [9], and Brunner [10]. The critical constants of normal alkanes with carbon numbers $n = 19 - 24, 26, 28, 30,$ and 36 have been measured by us using the pulse-heating technique with ultralow residence times [11,12]. This technique has been used in this work as well to measure the critical temperatures and pressures of tetracontane ($n = 40$), tetratetracontane ($n = 44$), and hexacontane ($n = 60$).

2. Experimental

2.1. Materials

The samples of the compounds studied were of commercial origin and used without any further purification. The sources, purities, and Chemical Abstracts Service Registry Numbers (CASRN's) are given in Table 1. Before and after the measurements of the critical properties, PMR spectra of the samples were obtained using a Bruker DRX 400 MHz NMR spectrometer. The spectra taken before and after the measurements of the critical parameters were completely identical so that the thermal decomposition of the samples during the experiments was small enough.

2.2. Method

The critical temperatures and the critical pressures of heavy normal alkanes were measured using the pulse-heating method discussed in detail elsewhere [13–17]. The method is based on the phenomenon of liquid superheat [18–20]. It is well known that a liquid can be heated at a given pressure above the vapor–liquid equilibrium temperature and exist in a metastable (superheated) state. Under the conditions of rapid heating a metastable liquid boils up at the temperature of the attainable superheat (spontaneous boiling-up). The critical point is the end point both on the vapor–liquid equilibrium line and on the line of the attainable superheat. Consequently, the critical pressure and the critical temperature can be determined by measuring the pressure dependence of the temperature of the attainable superheat. This dependence

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A	Filippov's similarity parameter
A_1	Riedel's parameter
c	specific heat capacity at constant pressure
c_p^0	specific heat capacity in the ideal-gas state
d	diameter of probe
J	rate of bubble nucleation
k	Boltzmann constant
L	specific enthalpy of evaporation
M	molar mass
n	number of carbons in a molecule of normal alkanes
p	pressure
R	universal gas constant
T	temperature
t	time
t^*	time from the beginning of a heating pulse to the moment of boiling-up
Z_C	critical compressibility factor
Greek symbols	
β	critical index
θ	temperature perturbation
λ	thermal conductivity
$1/\pi_0$	correction factor for the critical pressure
ρ	density
$1/\tau_0$	correction factor for the critical temperature
ω	acentric factor
Subscripts	
c	critical state
m	maximum (amplitude) value
nb	normal boiling
r	reduced value
s	saturation state
vp	vapor
Superscript	
m	measured value
$*$	attainable superheat

is measured in the pulse-heating method with the help of a wire probe heated by electric current pulses.

Briefly, a liquid under study filled a thin-walled Teflon cup; the pressure outside the cup was created by a press and measured by a dial gauge. If the compound under study was a liquid at room temperature, the measuring chamber containing the Teflon cup was at room temperature too. If the melting point of the compound under investigation was higher than room temperature, the chamber was maintained at a temperature 10–15 K above the melting temperature. A platinum wire probe, 2×10^{-3} cm in diameter and 1–3 cm in length, was placed in the liquid. The probe was heated by pulses of electric current in such a way that by the end of a pulse, the probe and the thin liquid layer near it were heated to the temperature of spontaneous boiling-up (attainable superheat). The time from the start of a pulse to the moment of boiling-up t^* was from 0.03 to 1.00 ms. At the moment of boiling-up a probe temperature perturbation Θ arises from an abrupt change of the conditions of heat transfer from the probe to the liquid. The probe temperature was determined from its resistance at that moment. The probe temperature perturbation may be both positive and negative. The pressure in the liquid increased until the negative temperature perturbation dropped to the level of the apparatus sensitivity (1×10^{-3} K). This pressure was taken to be equal to the measured value of the critical pressure p_c^m, and the temperature of the attainable superheat at this pressure was taken to be equal to the measured value of the critical temperature T_c^m.

Table 1
Molar-fraction x purities of compounds used in critical point measurement according to the suppliers' certificates of analysis (GC).

Compound	CASRN[a]	Supplier	10^2x
n-Tetracontane	4181-95-7	Fluka	98.7
n-Tetratetracontane	7098-22-8	Aldrich	98.9
n-Hexacontane	7667-80-3	Aldrich	98.4

[a] Chemical abstracts service registry number.

2.3. Calculation of the correction factors

The critical pressure and the critical temperature measured in the course of the pulse-heating experiments are always lesser than the true critical properties. The true critical pressure p_c and temperature T_C of a stable compound are calculated by the following equations:

$$p_c = p_c^m/\pi_o, \quad T_c = T_c^m/\tau_0, \tag{1}$$

where $1/\pi_0$ and $1/\tau_0$ are correction factors. The quantities π_0 and τ_0 have the sense of the theoretical values of the reduced pressure $p_r = p/p_c$ and the reduced temperature $T_r = T/T_c$ at which the amplitude of the negative temperature perturbation decreases to the level of the apparatus sensitivity (1×10^{-3} K). A method of calculating the correction factors has been given in a previous publication [13]. In this work we give an important improvement of the calculating method which was first published in [17]. The key quantity in the calculation of the correction factors is the difference of the temperature of the attainable superheat and the saturation temperature at a given pressure. Earlier both quantities in the vicinity of the critical point were approximated in (T, p) coordinates by straight lines. It is a rough but satisfactory approximation for low-molar-mass compounds with comparatively small acentric factors because the correction factors $1/\pi_0$ and $1/\tau_0$ only slightly exceeded 1 for such substances. However, for compounds with greater acentric factors, for instance, for heavy *n*-alkanes studied in this work, this approximation becomes too rough.

A thermophysical problem of boiling-up of a liquid on the surface of a wire probe heated by an electric current pulse was solved by Pavlov [21–23]. According to this solution, the amplitude of the negative temperature perturbation Θ_m is given by [13]

$$\Theta_m = 4q_1\left(\ln D + 1 - D\right)/\rho c d G_T \dot{T} \tag{2}$$

where q_1 is the heat flow density on the wetted surface of the probe:

$$q_1 = 2\dot{T}\left(t^*\lambda'\rho'c'/\pi\right)^{1/2}. \tag{3}$$

The temperature of the liquid near the probe changes from the temperature of boiling-up T^* to the temperature in the measuring chamber T_0. To take into account the temperature dependence of the liquid properties they are taken in Eq. (3) at the average temperature $(T^* + T_0)/2$; q_2 is the heat flow normalized to the length of the perimeter of a vapor bubble growing on the probe:

$$q_2 = \left(2\lambda\lambda'\right)^{1/2}\left(T^* - T_s\right). \tag{4}$$

$$D = 2\left[\left(\pi q_2 G_T \dot{T} \rho'' L\right)^{1/2}/q_1\right] - 1. \tag{5}$$

In Eqs. (2)–(5) ρ, c, and λ are the density, specific heat capacity at constant pressure, and thermal conductivity. Values marked with one prime pertain to the liquid, with two primes to the vapor, and with no prime to the probe material (platinum). L is the specific enthalpy of evaporation, $\pi = 3.1416$, d is the diameter of the probe, $\dot{T} = (T^* - T_0)/t^*$ is the mean rate of heating, T_S is the saturation