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Estimation of the Critical Constants of Long-Chain Normal Alkanes

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Correlations between the critical constants of normal alkanes and the number of carbon atoms in a molecule have been considered. In an approximation of a self-consistent field for a polymeric fluid, an equation of state of the van der Waals type has been written, and the dependences of the critical constants of chain molecules on the number of mers have been obtained. It has been found that for an infinitely long alkyl chain, the limiting values of the critical temperature, the critical pressure, and the critical density are equal to, respectively, 1135 K, 0 MPa, and 0 $kg \cdot m^{-3}$. A method of pulse heating of a wire probe immersed in the substance under investigation has been used to measure the dependence of the temperature of the attainable superheat T^* of low-density polyethylene on the pressure p and the duration of heating pulse t^*. Extrapolation has been used to obtain an estimation of the attainable-superheat temperature of polyethylene $T^*(p=0, t^*=0) = 1175$ K, which can be treated as the "critical" temperature of polyethylene.

KEY WORDS: alkanes; chain molecules; critical parameters.

1. INTRODUCTION

The measurement of the critical constants of long-chain normal alkanes is difficult because of their thermal decomposition. By now the critical temperature and pressure of n-alkanes have been measured for tetracosane [1], and the critical density for octadecane [2]. We believe that the pulse-heating method in the form used by us [3] will make it possible to measure the critical temperature and pressure of normal alkanes with a number of carbon atoms n up to 35–40. A further advance along the scale

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n will require modification of this method or development of a new procedure. The situation with measurements of the critical density is even more complicated. Therefore, of fundamental importance are calculation methods to determine critical properties.

We consider only methods based on a correlation between critical constants and the number of carbon atoms and make an estimation of the critical properties of an infinitely long alkyl chain. Usually, such an estimation is made in the following way. A function of the number of carbon atoms n that approximates experimental data is written and then n tends to infinity. With such an extrapolation one should bear in mind that the accuracy of approximation of experimental data cannot serve as a criterion of the accuracy of estimation of a limiting value, because it is quite evident that one can construct a function which will satisfactorily describe the results of measurements in a given interval of n but yield absurd values outside this interval. Of greater importance is the theoretical validity of the choice of the approximating function. Unfortunately, none of the approximations used at present, except the approximation of Kurata an Isida [4], has good substantiation. Nevertheless, we consider some of them.

2. CURRENT METHODS FOR ESTIMATING CRITICAL PROPERTIES OF *n*-ALKANES

2.1. Critical Temperature

Kreglewski and Zwolinski [5] have proposed the following equation for the critical temperature T_c of n-alkanes:

$$\lg(T_c^\infty - T_c) = a - bn^{2/3} \tag{1}$$

where T_c^∞ is the limiting value of the critical temperature at $n \to \infty$. Here and below a, b, c, d,... are constants pertaining only to a certain equation. Although Kreglewski and Zwolinski thought that the value of T_c^∞ had no physical meaning, thereafter it was considered as the critical temperature of an infinitely long alkyl chain [6]. Making use of the data for $n = 3$–18, Tsonopoulos [6] found $T_c^\infty = 959.88$ K, and Bolotin et al. [7] obtained $T_c^\infty = 961$ K. Later Bolotin and Shelomentsev [8] gave up the degree 2/3 of n and, taking into account the data of Smith et al. [9], obtained the following equation:

$$\lg(955.4 - T_c) = 2.96 - 0.0953n^{0.656} \tag{2}$$

that is, $T_c^\infty = 955.4$ K. The critical temperatures of n-alkanes calculated using Eq. (2) are given in Table I.

Table I. Comparison of Experimental[a] and Calculated Critical Temperatures of *n*-Alkanes

	Temp. (K)						
n	T_c (exp)	Eq. (2)	Eq. (4)	Eq. (5)	Eq. (7)	Eq. (8)	Eq. (43)
1	190.55			192.36			
2	305.5			305.89			
3	369.99			370.35			
4	425.16			424.42			
5	469.7	470.02		469.07			
6	507.4	507.40		506.87	506.31		
7	540.3	540.03		539.73	540.16		
8	568.8	568.89		568.70	569.47		
9	594.7	594.65		594.55	595.33		
10	617.9	617.81	615.94	617.81	618.46		614.0
11	638.4	638.78	638.67	638.97	639.38		638.2
12	658.8	657.86	659.12	658.32	658.49	655.44	659.4
13	676.0	675.29	677.39	676.11	676.06	675.62	678.0
14	691.8	691.29	693.86	692.66	692.33	693.40	694.7
15	707.5	706.02	708.81	708.02	707.48	709.19	709.6
16	722.4	719.62	722.43	722.33	721.64	723.30	723.1
17	735.9	732.21	734.89	735.87	734.95	735.98	735.4
18	747.7	743.89	746.33	748.36	747.50	747.44	746.6
19	755.3	754.76	756.87	760.15	759.37	757.85	757.0
20	767.5	764.90	766.61	771.32	770.63	767.73	766.6
21	777.6	774.35	775.64	781.87	781.35	776.02	775.4
22	785.6	783.20	784.04	791.88	791.56	784.01	783.7
23	789.7	791.49	791.88	801.37	801.32	791.37	791.4
24	799.8	799.26	799.19	810.38	810.66	798.18	798.7
50		902.99	898.48	948.40	971.80	884.28	901.9
100		945.28	953.13	1027.03	1123.97	927.10	970.2
1,000		955.40	1008.33	1021.00	1629.48	967.40	1082.8
10,000		955.40	1014.20	1021.00	2134.99	971.53	1118.4
∞		955.4	1014.86	1021.00	∞	971.99	1134.9
Average deviation (%)[b]		0.145	0.170	0.075	0.085	0.184	0.220
Carbon span		5–16	10–24	2–18	6–18	12–24	10–24

[a] The experimental values are from Refs. 1, 11, and 31.

[b] Deviation $= |T_c^{\text{exp}} - T_c^{\text{calc}}|/T_c^{\text{exp}}$.

Schonhorn [10] presented the dependence of the critical temperature of *n*-alkanes as

$$T_c^{-1} = (T_c^{\infty})^{-1} + bn^{-1} \tag{3}$$

Equation (3) describes quite well experimental data for $n > 10$. Schonhorn, at $n = 11$–20, obtained $T_c^{\infty} = 1031$ K. We, using the results of measurements of Rosenthal and Teja [11] and our own data [1], for $n = 10–24$, obtained the equation

$$T_c^{-1} = 0.98536\ 10^{-3} + 0.63817\ 10^{-2} n^{-1} \tag{4}$$

According to Eq. (4) $T_c^\infty = 1014.86$ K.

For the estimation of T_c^∞ Somayajulu [12] made use of the Ambrose equation [13]

$$T_b/(T_c - T_b) = a + bn \tag{5}$$

where T_b is the temperature of normal boiling, and a modified Kreglewski equation

$$\lg(T_b^\infty - T_b) = a - bn^{2/3} - cn - dP \tag{6}$$

where P is the Platt number [14]. Equations (5) and (6) are accurate enough for $n = 1–18$ (see Table I) but predict an unusual behavior of the critical temperature: at first with increasing n it increases, reaches a maximum value at $n \simeq 200$, and then decreases to $T_c^\infty = 1021$ K. It is necessary to point out that although such an estimation gives quite a reasonable value of T_c^∞, Ambrose himself has never stated that his equation is valid for heavy alkanes. In accordance with Eq. (5) at $n \to \infty\, T_b = T_c$, i.e., the critical pressure of an infinitely long alkyl chain is equal to atmospheric pressure. This conclusion is open to question, taking into consideration the diffuculties of transition of long-chain molecules into a vapor phase.

Fisher [15] proposed the following equation:

$$T_c = 112.95 + 505.51 \lg n \tag{7}$$

that describes well enough the results of measurements for $n = 6–18$. This equation leads to an infinite temperature at $n \to \infty$.

One can also propose other approximating functions. Thus, at $n > 10$ the equation

$$\lg T_c = 2.98766 - 2.05349 n^{-1} \tag{8}$$

works fairly well (Table I). For this case $T_c^\infty = 971.99$ K.

2.2. Critical Pressure

For correlation of the critical pressure Kreglewski and Zwolinski [5] have suggested the following equation:

$$\lg p_c = a - bn^{2/3} \tag{9}$$

Tsonopoulos [6], after processing the results of measurements for $n = 3$–14, has obtained the equation

$$\ln p_c = 2.01718 - 0.274281 n^{2/3} \qquad (10)$$

Bolotin and Shelomentsev [8] have suggested an equation that is similar in form,

$$\lg(0.98692 p_c) = 0.8317 - 0.11 n^{0.656} \qquad (11)$$

The Ambrose equation [16] is also well-known,

$$p_c = 0.101325\ 10^3\ M/(0.34 + 0.227n)^2 \qquad (12)$$

Fisher [17] recommends using the equation

$$p_c^{-1} = 0.11032 + 0.03602n \qquad (13)$$

Equations (9)–(13) predict the zero critical pressure of an infinitely long alkyl chain. Some authors, however, consider this pressure nonzero. For instance, Teja and co-workers [18] have proposed the following equation for the critical pressure:

$$\ln(p_c - p_c^{\infty}) = a - bn^c \qquad (14)$$

where $p_c^{\infty} = 0.84$ MPa. For calculating the critical pressure of *n*-alkanes, Somayajulu [12] recommends using an equation of the type

$$[M/(p_c - p_c^{\infty})]^{1/2} = a + bn + cP + dn^{1/2} \qquad (15)$$

where the limiting value of the critical pressure is equal to atmospheric, i.e., $p_c^{\infty} = 0.101325$ MPa.

2.3. Critical Density

The question of dependence of the critical density on the number of carbon atoms is more complicated. Due to a lack of experimental data during many years investigators held to the idea that the critical density almost did not depend on n. And only recently have Teja and co-workers [2] shown that the critical density begins to decrease when $n > 7$.

The Lydersen [19], Tsonopoulos [6], and Fisher [17] equations, identical in form,

$$\rho_c = M/(a + bn) \qquad (16)$$

predict a slow increase in ρ_c with increasing n and a limiting value of the critical density $\rho_c^\infty = 235\text{–}255\ \mathrm{kg \cdot m^{-3}}$. A somewhat more complicated equation of Kreglewski and Zwolinski,

$$\rho_c = M/[a + b(n + n^{2/3})] \tag{17}$$

also gives a finite and nonzero ciritical density of an infinitely long alkyl chain.

The Somayajulu equation [12]

$$\rho_c = M(aY + bY^2 + cY^3 + dY^4 + eY^5) \tag{18}$$

where $Y = p_c/RT_c$, leads to an infinite critical density at $n \to \infty$.

The equation of Teja et al. [18]

$$\rho_c = M/(a + bn^{1.16535}) \tag{19}$$

predicts a zero limiting value of ρ_c.

3. CORRELATIONS BASED ON THE THEORY OF POLYMERIC SOLUTIONS IN AN APPROXIMATION OF A SELF-CONSISTENT FIELD

On the basis of the Flory theory of polymeric solutions, Kurata and Isida [4] have obtained the following equations:

$$T_c^{-1} = a + b(0.5y^{-1} + y^{-1/2}) \tag{20}$$

$$p_c T_c^{-1} = c\{\ln[1 + y^{-1/2}] - (2y^{1/2} - 1)/2y\} \tag{21}$$

$$\rho_c = M/y(1 + y^{1/2}) \tag{22}$$

where y is the number of cells occupied by a chain molecule in a lattice model of liquid. Kurata and Isida assumed $y = n^{2/3}$ from the condition of constancy of the critical density of n-alkanes. The results of experiments available at that time pointed to this. However, as already noted, the latest measurements of Teja et al. [2] show that for $n > 7$ the critical density decreases, therefore the arguments of Kurata and Isida cannot be considered convincing. On the other hand, Eq. (20) with $y = M$, where M is the molar mass, beginning from the work of Schultz and Flory [20], is widely and successfully used for describing the critical solution temperature of (polymer + solvent) mixtures. A lot of examples of using Eq. (20) are given in Ref. 21. Let $y = n$, where n is the number of mers in a chain molecule equal in the case of *n*-alkanes to the number of carbon atoms. Then Eqs. (20)–(22) take the form

$$T_c^{-1} = a + b(0.5n^{-1} + n^{-1/2}) \tag{23}$$

$$p_c T_c^{-1} = c\{\ln[1 + n^{-1/2}] - (2n^{1/2} - 1)/2n\} \tag{24}$$

$$\rho_c = (d + gn)/n(1 + n^{1/2}) \tag{25}$$

Dependences of the critical constants on the number of mers, which are quite similar and at $n \gg 1$ coincide in form with Eqs. (23)–(25), can be obtained in an approximation of a self-consistent field. Let us consider a volume V in wich N monomeric molecules are located. The free energy of this system is represented as

$$F_{\mathrm{m}} = F_{\mathrm{mvol}} + F_{\mathrm{mid}} \tag{26}$$

Here F_{mvol} is the part of the free energy connected with the volume interaction of molecules, and F_{mid} is the free energy of an ideal gas [22]:

$$F_{\mathrm{mid}} = -kTN \ln(eV/N) + Nf(T) \tag{27}$$

where T is the temperature, k is the Boltzmann constant, e is the base of a natural logarithm, and $f(T)$ is some temperature function. Let us assume that polymerization has taken place in a volume V, and chain molecules have formed, each of which contains n mers. The free energy of a polymeric fluid is written in much the same way as in Eq. (26):

$$F_{\mathrm{p}} = F_{\mathrm{pvol}} + F_{\mathrm{pid}} \tag{28}$$

Within the framework of the model of a self-consistent field, it is suggested that the contribution of volume interactions to the free energy of a system consisting of chain molecules is the same as in a system of broken links [23], i.e., $F_{\mathrm{pvol}} = F_{\mathrm{mvol}}$. After polymerization the number of particles moving independently decreased by a factor of n, therefore, the folowing equation is valid for F_{pid}:

$$F_{\mathrm{pid}} = -kT(N/n) \ln(eVn/N) + (N/n) f_1(T) \tag{29}$$

By solving Eqs. (26)–(29) simultaneously, we obtain the pressure of a polymeric fluid:

$$p_{\mathrm{p}} = -(\partial F_{\mathrm{p}}/\partial V)_{\mathrm{T}} = p_{\mathrm{m}} - kTN/V + kTN/Vn \tag{30}$$

The result obtained is clear: the difference of the pressure of a polymeric fluid from the pressure of a fluid of mers consists in replacing the ideal-gas pressure caused by the independent motion of mers whose concentration is equal to N/V with the ideal-gas pressure of chains whose concentration is equal to N/Vn.

The pressure of a monomeric fluid can be described by any of the well-known equations of state. Let us take the van der Waals equation:

$$p_m = kTN/(V - b_* N) - a_* N^2/V^2 \tag{31}$$

The constants a_* and b_* satisfy the conditions

$$p_{cm} = a_*/27b_*^2, \qquad V_{cm} = 3b_* N, \qquad kT_{cm} = 8a_*/27b_* \tag{32}$$

where p_{cm}, V_{cm}, and T_{cm} are the critical constants of a fluid of mers. Then the equation of state of a polymeric fluid can be written as

$$p_p = kTN/(V - b_* N) - a_* N^2/V^2 - kTN/V + kTN/Vn \tag{33}$$

At the critical point the following conditions are fulfilled:

$$(\partial p/\partial V)_T = 0, \qquad \text{and} \qquad (\partial^2 p/\partial V^2)_T = 0 \tag{34}$$

By solving Eqs. (33) and (34) simultaneously, we obtain for $n \gg 1$

$$T_c = (27/8)\, T_{cm}[1 - (3/n)^{1/2}] \tag{35}$$

$$p_c = p_{cm}(3/n)^{3/2} \tag{36}$$

$$\rho_c = \rho_{cm}(3/n)^{1/2} \tag{37}$$

It is not difficult to notice that these relationships give the same dependence of the critical constants on the number of mers as Eqs. (23)–(25) in the case $n \gg 1$. Such a result is not unexpected, as the basis for the Flory theory is an approximation of a self-consistent field [23]. We also note that computer simulation has given a similar dependence of the critical density on the number of mers [24]: $\rho_c \sim n^{-1/2}$. Monte Carlo calculation of a phase diagram for a bead-spring polymeric model [25] has shown that the estimated critical temperatures for $n = 20, 50$, and 100 approximately satisfy Eq. (23).

If in a volume V only partial polymerization has taken place, and there has formed a polymer solution in its own monomer with a concentration $x = N_1/N$, where N_1 is the number of monomer molecules, we obtain an equation of state for a solution:

$$p = kTN/(V - b_* N) - a_* N^2/V^2 - kTN(1 - x)/V + kTN(1 - x)/Vn \tag{38}$$

Next, by solving Eqs. (38) and (34) simultaneously, we obtain at a low monomer concentration ($x \ll 1$) the following expressions for the critical constants of the solution:

$$T_c = (27/8)\, T_{cm}\{1 - [3(1/n + x)]^{1/2}\} \tag{39}$$

$$p_c = p_{cm}[3(1/n + x)]^{3/2} \tag{40}$$

$$\rho_c = \rho_{cm}[3(1/n + x)]^{1/2} \tag{41}$$

4. TEMPERATURE OF THE ATTAINABLE SUPERHEAT OF POLYETHYLENE

Additional information on the limiting value of the critical temperature of *n*-alkanes can be obtained by measuring the temperature of the attainable superheat of polyethylene. For low molecular weight liquids the temperature of the attainable superheat is the temperature of spontaneous boiling when nuclei of a vapor phase emerge as a result of density fluctuations. In the coordinates (pressure, temperature) the pressure dependence of the attainable-superheat temperature $T^*(p)$ is shown with a line lying close to the spinodal and ending at the critical point. The approximate equation

$$T^*(p = 0.1\ \text{MPa}) \simeq 0.9 T_c \tag{42}$$

is valid at atmospheric pressure [26].

One of the methods of measuring the temperature of the attainable superheat is the method of pulse heating of a thin wire probe immersed in the liquid under investigation [26–28]. The peculiarities of measuring the temperature of the attainable superheat of polymer melts, and the diagram of the apparatus are given in Ref. 29.

The probe, a platinum wire 0.002 cm in diameter and from 1 to 3 cm in length, is heated with pulses of electric current with a duration from 0.01 to 2–3 ms. The apparatus makes it possible to register against the background of continuous heating low-amplitude (more than 10^{-3} K) but sufficiently high-frequency perturbation of the probe temperature. The reason for such a perturbation of the temperature is the change of the conditions of heat transfer from the probe to the surrounding medium. In the case of low molecular weight liquids it is their boiling-up. For molten polymers one can also observe closely analogous perturbations of the probe temperature. The physical nature of these perturbations is not so evident as for low molecular weight liquids. We think that here we are dealing with the boiling-up of products of thermal decomposition of a polymer formed in the process of its pulse heating. In Ref. 30 polyethene glycols are used to illustrate that the mass content of the products of thermal decomposition by the moment of boiling-up is of the order of magnitude 0.1% at the same pulse duration t^* as in experiments with polyethylene.

We used a commercial-grade low-density polyethylene of make 10803–020. The properties of the polyethylene were as follows: the number-average molecular weight $\bar{M}_n = 3 \times 10^4$; the index of polydispersity $\bar{M}_w/\bar{M}_n = 20$, where $\bar{M}_w$ is the weight-average molecular weight; and the number of CH_3 groups for 100 carbon atoms was 2.3. About 1 g of polyethylene was placed in a glass cup 1.5 cm in diameter and evacuated under vacuum at a temperature of 450 K. Measurements of the temperature of the attainable superheat T^* were made during evacuation with the help of a probe immersed into the melt. When the value of T^* stopped changing, the evacuation was discontinued, and measurements of $T^*(t^*)$ dependence at different pressures p were carried out (Fig. 4). The pressure on the melt was created by argon. In the course of measurements argon probably dissolves in a polyethylene melt, which may shift the value of T^*. This effect was studied in a special experiment. It was shown that it was smaller than the apparatus sensitivity. $T^*(p)$ dependence was determined with a stepwise pressure increase up to a certain pressure p_1 above which the characteristic perturbation of the probe temperature was no longer resolved. For low molecular weight thermally stable liquids and mixtures, the values of $p_1(t^* > 0.1 \text{ ms})$ is quite close to the critical pressure [1, 3]. We assume that it is also valid for (low molecular weight substance + polymer) mixtures. The dependences of the temperature of the attainable superheat and the pressure p_1 on the pulse duration are most probably caused by the thermal decomposition of polyethylene. An increase in the t^* value produces the same effect on the values of T^* and p_1 as the introduction of a low molecular weight component into the initial substance [29, 30]. Therefore, a certain concentration of the products of thermal decomposition C can be attributed to every curve $T^*(p)$ at a fixed heating time t^*, and the values of p_1 and $T^*(p_1)$ may be considered close to the critical constants of the solution. Then by extrapolating the line of the critical points of the solutions to zero concentration C (i.e., to $t^* = 0$), with allowance for the assumption that the critical pressure of a polymer is equal to zero, we obtain an estimation for the critical temperature of polyethylene (Fig. 4). Such an extrapolation gives a value of $T^*(p = 0, t^* = 0) = (1175 \pm 20)$ K when using a polynomial of degree 2. This value is believed to be close to the critical temperature of an infinitely long alkyl chain.

5. DISCUSSION

The authors of the equations considered in Section 2 believed that their main task was to describe the available experimental data as precisely as possible and predict the critical properties of heavier members of homologous series by prudent extrapolation. The estimation of the limiting values of the critical constants interested them secondarily or not at all. On the contrary, our aim is to obtain equations giving correct dependence of the critical properties on the number of mers for $n \gg 1$ and estimate the critical constants of an infinitely long alkyl chain. When using Eqs. (35)–(37) one should bear in mind that there is a difference between the structure of a polymeric link and that of a molecule of the lowest term of a homologous series. For *n*-alkanes these are ($-CH_2-$) and CH_4. Therefore one should not expect that by substituting the critical constants of methane instead of T_{cm}, p_{cm}, and ρ_{cm} into Eqs. (35)–(37), we obtain correct values of the critical properties of other *n*-alkanes.

Figures 1–3 show the available results of measurements of the critical constants of *n*-alkanes. Use was made of the following sources. For the critical temperature and pressure, $n = 1$–4 [31], $n = 5$–18 [11], and $n = 19$–24 [1]. For the critical density, $n = 1$–18 [12]. The straight line in Fig. 1 is the calculated T_c from equation

$$T_c = 1134.9 - 1647.23n^{-1/2} \tag{43}$$

The form of this equation does not differ greatly from Eq. (35), but Eq. (43) describes experimental data better than Eq. (35). The main feature that unites Eqs. (35) and (43) is the same dependence of the critical temperature on the number of mers: $T_c \sim n^{-1/2}$. In accordance with Eq. (43) the limiting value of the critical temperature of an infinitely long alkyl chain is equal to 1135 K. This value is somewhat higher than those given by the equations considered in Section 2 and sufficiently close to the temperature of attainable superheat of polyethylene $T^*(p = 0, t^* = 0) = (1175 \pm 20)$ K determined in Section 4. The difference between these values should not rouse surprise. Both of them have been obtained by essentially distant extrapolation. Besides, the polyethylene we used consisted of branched rather than linear molecules. The choice of branced polythylene is caused by the experimental technique limitation to reasonably high viscosities. Branched (i.e., low-density) polyethylenes have much lower melt viscosities than linear polyethylenes of the same molecular weight [32].

The critical temperatures calculated by Eq. (43) and the equations discussed in Section 2 are compared with the experimental data in Table I. Table I shows that the Somayajulu equation [Eq. (5)] is the best one to describe the available experimental data in its own regression interval.

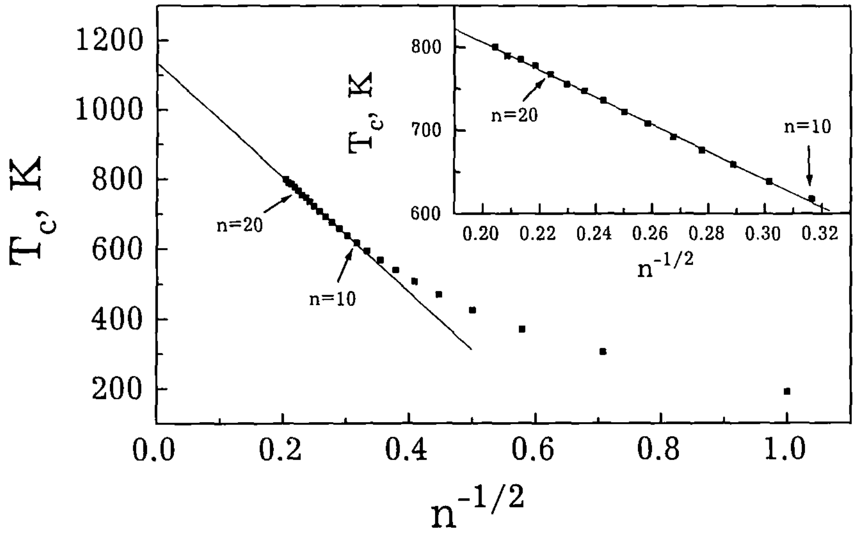

Fig. 1. The critical temperature of *n*-alkanes. Solid line: $T_c = 1134.9 - 1647.23n^{-1/2}$.

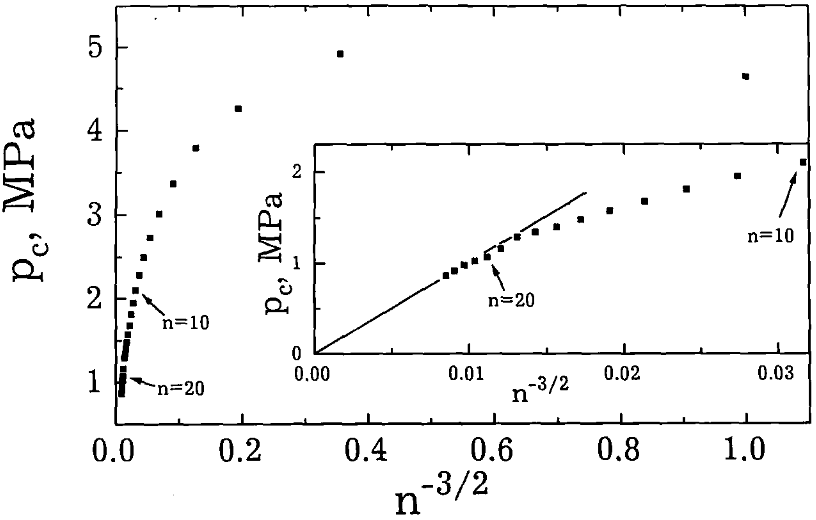

Fig. 2. The critical pressure of *n*-alkanes.

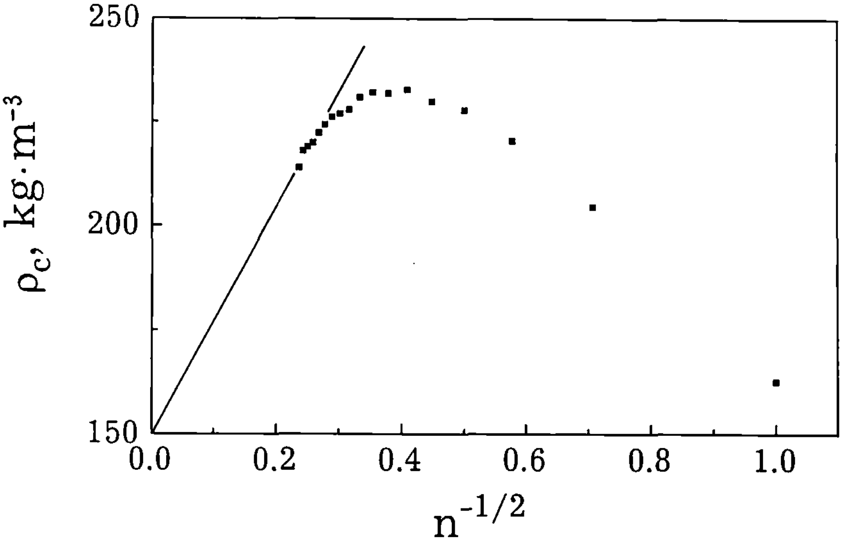

Fig. 3. The critical density of *n*-alkanes.

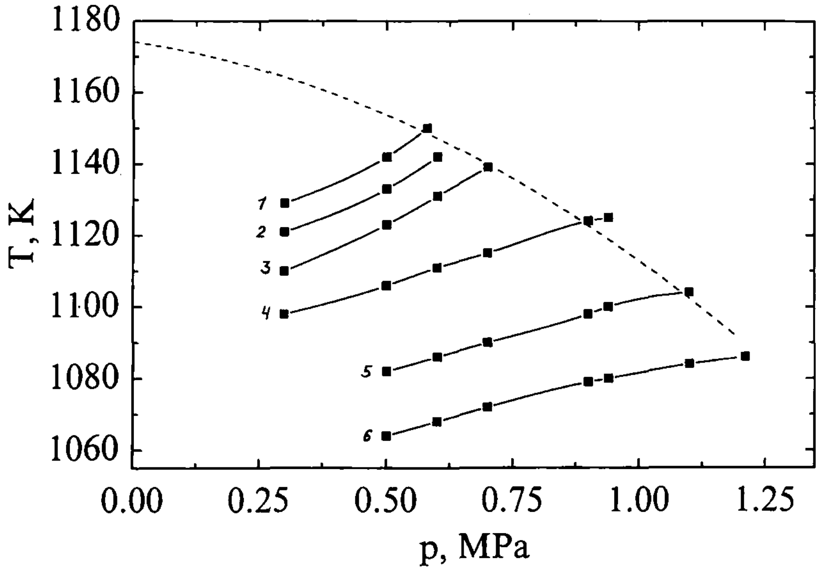

Fig. 4. Pressure dependences of the temperature of the attainable superheat of polyethylene at six heating times t^* (μs): 1–40, 2–70, 3–120, 4–200, 5–440, and 6–790. The last points show the values of $T^*(p_1)$. Extrapolation of these values to $p_1 = 0$. (dashed line) gives an approximation for the critical temperature of polyethylene.

However, at $n = 19–24$ this equation predicts higher values of the critical temperature than those given by our experiments [1]. For $n = 24$ the difference $|T_c^{\exp} - T_c^{\text{calc}}|$ achieves 10 K. This exceeds the measurements error, which in the pulse-heating method is 0.01 T_c and, for $n = 24$, is equal to ± 8 K. The Fisher equation [Eq. (7)] for $n = 19–24$ also gives higher values of T_c than experimental ones. The values of the critical temperatures for $n = 19–24$ that are closer to experimental ones are obtained from the equation of Bolotin and Shelomentsev [Eq. (2)]. Naturally, Eqs. (4), (8), and (43) as a whole describe the interval $n = 19–24$ better as the experimental data for this interval were used in determining the coefficients of these equations. It is necessary to note that Eqs. (35)–(37), and therefore Eq. (43) too, are valid only for sufficiently long molecules ($n \gg 1$).

Figure 2 shows that Eq. (36) for the critical pressure begins to work at $n > 18–20$. Equation (37) for the critical density is obviously valid for even larger n. The lack of experimental data on these critical properties of heavy n-alkanes does not make it possible yet to judge how well Eqs. (36) and (37) describe this interval of n. We believe that Eqs. (36) and (37) predict the correct limiting values of the critical pressure and the critical density. Monte Carlo simulation of Sheng et al. [25] gives zero values for these quantities as well.

6. CONCLUSIONS

Equations (35)–(37) are valid not only for n-alkanes. The critical constants of any substance that consists of chain molecules at a large number of mers satisfy these relations. In particular, Eq. (36) was used by us for describing the results of measurement of the critical pressure of polyethene glycols from monoethene glycol to polyethene glycol with $\bar{M}_n = 600$ [33].

The value of the critical temperature of n-alkanes in the limit $n \to \infty$ falls by our estimations within an interval from 1000 to 1200 K. Of course, it is necessary to keep in mind that the estimation of the limiting value of the critical temperature by any of the formulae presented in this paper is approximate, as the interval of extrapolation is too large. A more accurate estimation requires direct measurements of the critical constants of heavy n-alkanes.

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