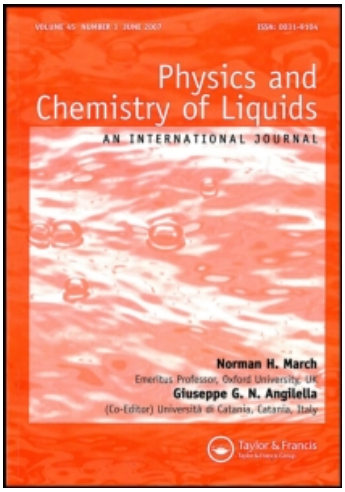

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Prediction Methods for the Critical Temperature of n -Alkanes

J. Amorós[a]
[a] Departamento de Física Aplicada, Universidad de Cantabría, Santander, Spain

Online publication date: 27 October 2010

To cite this Article Amorós, J.(2002) 'Prediction Methods for the Critical Temperature of n -Alkanes', Physics and Chemistry of Liquids, 40: 3, 269 — 275
To link to this Article: DOI: 10.1080/0031910021000004856
URL: http://dx.doi.org/10.1080/0031910021000004856

Phys. Chem. Liq., 2002, Vol. 40(3), pp. 269–275

Taylor & Francis
Taylor & Francis Group

PREDICTION METHODS FOR THE CRITICAL TEMPERATURE OF *n*-ALKANES

J. AMORÓS

Departamento de Física Aplicada, Universidad de Cantabria, 39005, Santander, Spain

(Received 27 February 2001)

The critical temperature of heavy *n*-alkanes is predicted from the behaviour corresponding to their melting temperature and from several empirical correlations. The prediction methods for the critical temperature of *n*-alkanes are reviewed, including the new experimental data currently available. The results obtained for T_c^{∞}, the limiting value of the critical temperature at $n \to \infty$, are compared. The calculated and experimental values of T_c coincide in the range $n = 5$–36 within the actual uncertainties.

Keywords: Critical temperature; Melting temperature; Alkane; Polyethylene

1. INTRODUCTION

Normal alkanes (*n*-alkanes) are linear hydrocarbon chains and are some of the simplest organic molecules. The main reasons for the great interest in *n*-alkanes are: (a) they are prototypical case of molecules with an articulated structure; (b) they are of prime importance for the petrochemical industries and (c) alkyl groups are essential for the function of many biological systems.

For low weight *n*-alkanes ($n \leq 9$), the critical properties are well known. From $n = 10$ and 11, the critical temperature exceeds the temperature of the onset of thermal decomposition, thus impeding the measurement of the critical properties. The greatest successes in the experimental determination of the critical temperature of thermally unstable alkanes are achieved by Teja and co-workers [1,2] (up to

ISSN: 0031-9104. Online ISSN: 1029-0451
DOI: 10.1080/0031910021000004856

$n = 18$) and Nikitin *et al.* [3,4] with $n = 19$–24 and $n = 26$, 28, 30 and 36 through a fast heating of the sample, so that significant thermal decomposition does not take place.

For $n > 36$, the critical properties of *n*-alkanes are not experimentally accessible. Their determination is viable from three possible procedures: (a) by means of an empirical extrapolation of the known results for low weight *n*-alkanes; (b) by semi-empirically starting from a liquid state theory such as the hole theory and (c) through the statistical mechanics by designing a microscopic model of the substance. Currently, the results of this last procedure are expressed using computer simulation methods.

In this work, the critical temperature of *n*-alkanes is calculated up to the infinite limit T_c^{∞} using the following two procedures. The first is founded on a systematic relation between the reduced melting temperature $T_{\mathrm{rm}} = T_m/T_c$, defined as the ratio between the melting and critical temperatures, and the number of carbon atoms n for $n \geq 18$. The second starts from equations taken from the literature for reproducing the critical temperature of *n*-alkanes. Such equations are applied to the full range of available experimental data and the characteristic parameters are modified to get an optimum fit. Finally we propose empirical equations whose agreement with experimental data is within the existing uncertainties. The value for T_c^{∞} is obtained in all the cases.

2. RESULTS AND DISCUSSION

Figure 1 shows the variation of the reduced melting temperature T_{rm} with the chain length n for the available experimental range. From methane through propane, T_{rm} decreases strongly. The normal melting temperatures of the *n*-alkanes exhibit the well-known odd-even effect. The melting temperature, of any alkane with an even number of carbon atoms is considerably higher than the averaged values of the two adjacent alkanes with an odd number of carbons. This peculiar behaviour is due to the distinct crystal structures describing the solid phase of all *n*-paraffins [5]. When n increases, this effect is weakened and is nearly non-existent for $n \geq 20$. From this chain length, T_{rm} is almost constant; $T_{\mathrm{rm}} \approx 0.404$ for the remaining range. This behaviour was assumed constant indefinitely so that the critical temperature is

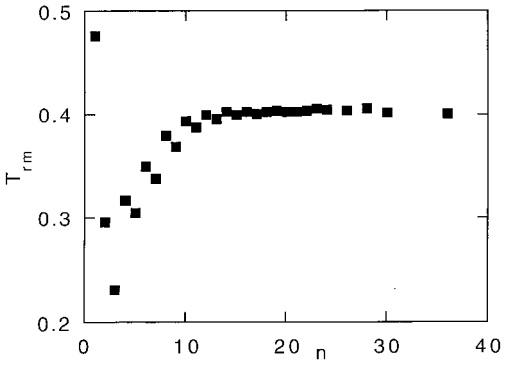

FIGURE 1 Reduced melting temperature T_{rm} versus the number of carbon atoms n for n-alkanes. ($n = 1$–36).

given approximately by $T_c = T_m/0.404$ for $n \geq 20$. Given that the melting temperature is known for many values of the chain length [5,6], this simple relation allows the calculation of the critical temperatures.

Since polyethylene is a normal alkane of essentially infinite molecular weight, its melting temperature ought to coincide with that corresponding to an infinite chain length. This proposal is confirmed by extrapolating the melting temperature of the n-alkanes [7]. The melting point of an extended chain polyethylene is 414.6 K [8]. The value obtained for the critical temperature from the approach presented here is $T_c^{\infty} = 1026.2$ K.

In contrast to T_{rm}, the reduced boiling temperature T_{rb} shows a smooth variation with the number of carbon atoms n (Fig. 2). This corroborates unambiguously the absence of any odd-even effect.

Several researchers have developed prediction methods for the critical temperature of n-alkanes. There is an excellent agreement up to $n = 18$. However, the new data of Nikitin *et al.* [4] for n-alkanes with $n > 18$ modified this status. We want to propose expressions for the inclusion of these new data. However, the procedure involves additional complications because the thermal instability implies considerably higher experimental errors. Given that no experimental research has confirmed those results, many researchers [9] did not use this work. However, we show that the usual procedures for predicting critical temperatures allow the inclusion of these data by smoothly changing some parameters.

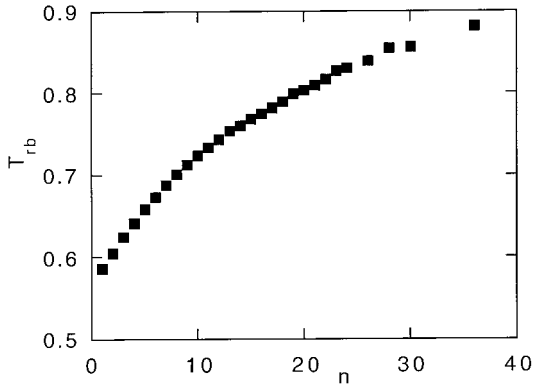

FIGURE 2 Reduced boiling temperature T_{rb} versus the number of carbon atoms for *n*-alkanes ($n = 1$–36).

Two types of equations have been proposed for the prediction of T_c. The first has a logarithmic form and its departure point is ascribed to Kreglewski and Zwolinski [10]:

$$\ln(y_\infty - y) = a - bn^{2/3} \tag{1}$$

where y is a property such as T_c or T_b and y_∞ is the limiting value of that property as $n \to \infty$. Tsonopoulos [11] and Teja *et al.* [12] employed this relation to correlate T_c of the *n*-alkanes for $n \geq 3$ and obtained respectively:

$$\ln(959.98 - T_c) = 6.81536 - 0.211145n^{2/3} \tag{2}$$

$$\ln(1143.8 - T_c) = 7.15908 - 0.303158n^{0.469609} \tag{3}$$

The second type of equation is of a polynomial nature and was formulated by Kurata and Isida [13] from a hole theory for normal paraffin liquids. In this context, the more important equations were formulated by Nikitin *et al.* [4], and Tsonopoulos and Tan [14] for $n \geq 5$ obtaining respectively

$$T_c = 1258.73 - 2654.38n^{-1/2} + 1992n^{-1} \tag{4}$$

$$10^4 \times T_c^{-1} = 9.4236 + 77.997(n+1)^{-1} - 41.304(n+1)^{-2} \tag{5}$$

Given that the critical temperature of *n*-alkanes have been measured with different errors, the experimental data have been weighted according to Ambrose and Tsonopoulos [15] for $n = 5$–18 and Nikitin *et al.* [4] for the remaining cases. Applying this procedure, we obtain the following relations:

$$\ln(911.43 - T_c) = 6.7929 - 0.23996n^{2/3} \quad (6)$$

$$\ln(1119.5 - T_c) = 7.1473 - 0.31506n^{0.469096} \quad (7)$$

$$10^4 \times T_c^{-1} = 9.4751 + 77.049(n+1)^{-1} - 37.448(n+1)^{-2} \quad (8)$$

The remaining equation is not reproduced here because it practically coincides with Eq. (4).

Although the earlier relations give acceptable results for T_c, a slight modification of the parameters would improve the fits. Therefore, we propose the following equations:

$$\ln(1010.6 - T_c) = 6.9834 - 0.28464n^{0.5503} \quad (9)$$

$$T_c = 1274.3 - 2846.3n^{-1/2} + 2127.5n^{-0.94} \quad (10)$$

$$10^4 \times T_c^{-1} = 9.3326 + 85.340(n+1)^{-1} - 33.486(n+1)^{-2} \quad (11)$$

The foregoing results suggest the expansion of T_c in a power series of $n^{-1/2}$ or alternatively of T_c^{-1} versus $(n+1)^{-1/2}$. In this context, we have obtained the following expressions:

$$T_c = 1123.0 - 619.90n^{-1/2} - 8666.5n^{-1} + 23554n^{-3/2} - 18739n^{-2} \quad (12)$$

$$10^4 \times T_c^{-1} = 9.5795 + 60.221(n+1)^{-1} + 66.833(n+1)^{-3/2} - 0.13013(n+1)^{-3} + 0.40841(n+1)^{-4} \quad (13)$$

Table I shows the results obtained for the earlier relations including the experimental errors Δ, the average absolute deviation (AAD), the maximum absolute deviation (MAD) and the percentage average deviation (PAD), defined as $100 \sum |T_c^{\exp} - T_c^{\text{calc}}|/T_c^{\exp}$ between experimental and calculated values.

Equations (12) and (13) give individual deviations which are smaller than the experimental errors in all the cases. Table I also lists T_c^{∞}. Other estimations for this quantity are 955.4 K [16]; 972.0, 1014.9

TABLE I Comparison of experimental and calculated critical temperatures of *n*-Alkanes

	$T_c(K)$										
n	*Exp.*	Δ	*Eq. (6)*	*Eq. (7)*	*Eq. (9)*	*Eq. (4)*	*Eq. (10)*	*Eq. (8)*	*Eq. (11)*	*Eq. (12)*	*Eq. (13)*
3	369.83	0.1	370.24	369.90	370.02						
4	425.12	0.1	424.44	424.99	424.79						
5	469.70	0.2	469.46	469.83	469.70	470.06	469.99	470.00	469.98	469.68	469.69
6	507.60	0.2	507.77	507.65	507.70	507.08	507.09	507.15	507.20	507.67	507.66
7	540.20	0.3	540.94	540.32	540.54	540.04	540.03	539.92	539.95	540.04	540.07
8	568.70	0.3	570.03	569.03	569.39	569.26	569.22	569.03	569.00	568.71	568.72
9	594.60	0.6	595.77	594.60	595.03	595.27	595.19	595.04	594.96	594.49	594.45
10	617.70	0.6	618.74	617.62	618.03	618.54	618.45	618.43	618.32	617.81	617.77
11	639.00	1	639.37	638.52	638.82	639.50	639.41	639.56	639.44	639.02	639.00
12	658.00	1	657.98	657.62	657.75	658.48	658.40	658.75	658.64	658.37	658.40
13	675.00	1	674.87	675.18	675.06	675.77	675.72	676.25	676.17	676.09	676.18
14	693.00	2	690.24	691.41	690.98	691.60	691.59	692.27	692.25	692.37	692.53
15	708.00	2	704.29	706.48	705.68	706.17	706.21	706.99	707.05	707.37	707.61
16	723.00	2	717.16	720.52	719.29	719.64	719.72	720.57	720.72	721.24	721.53
17	736.00	2	728.99	733.64	731.94	732.12	732.27	733.14	733.39	734.10	734.43
18	747.00	3	739.90	745.95	743.74	743.75	743.96	744.79	745.16	746.05	746.40
19	755.30	8	749.96	757.53	754.76	754.62	754.88	755.63	756.13	757.19	757.54
20	767.50	8	759.28	768.44	765.09	764.79	765.13	765.74	766.37	767.60	767.92
21	777.60	8	767.92	778.76	774.78	774.35	774.76	775.20	775.96	777.34	777.62
22	785.60	8	775.94	788.52	783.90	783.36	783.84	784.05	784.96	786.49	786.70
23	789.70	8	783.41	797.78	792.49	791.86	792.41	792.36	793.42	795.09	795.21
24	799.80	8	790.36	806.58	800.59	799.91	800.53	800.18	801.39	803.20	803.20
26	816.00	12	802.91	822.93	815.51	814.78	815.55	814.50	816.01	818.09	817.81
28	824.00	12	813.89	837.83	828.92	828.24	829.16	827.31	829.12	831.45	830.81
30	843.00	12	823.54	851.46	841.02	840.51	841.57	838.81	840.93	843.50	842.46
36	872.00	13	890.34	886.27	871.10	871.67	873.15	867.29	870.30	873.58	871.04
MAD			25.72	14.27	4.917	4.240	5.158	4.709	5.119	7.446	6.811
AAD			5.759	2.945	1.447	1.613	1.527	1.545	1.305	1.307	1.222
PAD(%)			0.7356	0.3679	0.1949	0.2180	0.2056	0.2038	0.1740	0.1680	0.1572
T_c^{∞}			911.43	1119.5	1010.6	1258.7	1274.3	1055.4	1071.5	1123.0	1043.9

and 1143.8 K [17]; 1021 K [18] and 1620 K [19]. This data collection seems to suggest a value in the range 970–1070 K. The fit of Nikitin *et al.* (Eq. 4) gives a number excessively high, but the introduction of higher powers in *n* (Eq. 12) considerably improves the result.

3. CONCLUSIONS

In this work, several correlations were developed for the critical temperature of *n*-alkanes. The first is based on the universal behaviour

given by corresponding states law. The remaining ones extend the available experimental correlations in this field, and give a good agreement with the available experimental data, considering the errors involved in the measurements. The critical temperature of *n*-alkanes in the limit $n \to \infty$ has a value around 1020 K.

References

[1] R.L. Smith, A.S. Teja and W.B. Kay (1987). *AlChE J.*, **33**, 232.
[2] D.J. Rosenthal and A.S. Teja (1989). *AlChE J.*, **35**, 1829.
[3] E.D. Nikitin, P.A. Pavlov and N.V. Bessonova (1994). *J. Chem. Thermodyn.*, **26**, 177.
[4] E.D. Nikitin, P.A. Pavlov and A.P. Popov (1997). *Fluid Phase Equilibria*, **141**, 155.
[5] M.G. Broadhurst (1962). *J. Res. Nat. Bur. Stand.*, **66A**, 241.
[6] G.R. Somayajulu (1990). *Int. J. Thermophys.*, **11**, 555.
[7] M.G. Broadhurst (1966). *J. Res. Nat. Bur. Stand.*, **70A**, 481.
[8] T. Arakawa and B. Wunderlich (1967). *J. Polym. Sci. Pt. C*, **16**, 653.
[9] E.W. Lemmon and A.R.H. Goodwin (2000). *J. Phys. Chem. Ref. Data*, **29**, 1.
[10] A. Kreglewski and B.J. Zwolinski (1961). *J. Phys. Chem.*, **65**, 1050.
[11] C. Tsonopoulos (1987) *AlChE J.*, **33**, 2080.
[12] A.S. Teja, R.J. Lee, D. Rosenthal and M. Anselme (1990). *Fluid Phase Equilibria*, **56**, 153.
[13] M. Kurata and S. Isida (1955). *J. Chem. Phys.*, **23**, 1126.
[14] C. Tsonopoulos and Z. Tan (1993). *Fluid Phase Equilibria*, **83**, 127.
[15] D. Ambrose and C. Tsonopoulos (1995). *J. Chem. Eng. Data*, **40**, 531.
[16] N.K. Bolotin and A.M. Shelomentsev (1991). *Phys. Liquid State* (*Kiev*), **19**, 75.
[17] E.D. Nikitin, P.A. Pavlov and P.V. Skripov (1996). *Int. J. Thermophys.*, **17**, 455.
[18] G.R. Somayajulu (1991). *Int. J. Thermophys.*, **12**, 1039.
[19] C. Vega and A. López Rodriguez (1996). *J. Chem. Phys.*, **105**, 4223.