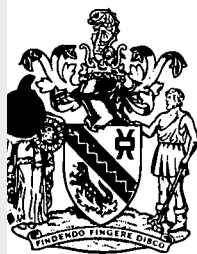


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**NORMAL MELTING POINTS, BOILING
POINTS AND CRITICAL POINTS OF
n-ALKYL ESTERS OF MONOBASIC
n-ALKANOIC ACIDS**

(APPROVED FOR ISSUE JANUARY 1971)

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NORMAL MELTING POINTS, BOILING POINTS AND CRITICAL
POINTS OF *n*-ALKYL ESTERS OF MONOBASIC
n-ALKANOIC ACIDS

1. INTRODUCTION

The liquids for which data are presented in this Item are the normal (i.e. straight chain) alkyl esters of the normal monobasic alkanolic acids (i.e. monocarboxylic acids) and are listed below.

- (a) Normal alkyl formates (methanoates), Table I.
- (b) Normal alkyl acetates (ethanoates), Table II.
- (c) Normal alkyl propionates (propanoates), Table III.
- (d) Normal alkyl butyrates (butanoates), Table IV.
- (e) Normal alkyl valerates (pentanoates), Table V.
- (f) Normal alkyl caproates (hexanoates), Table VI.
- (g) Normal alkyl oenanthates (heptanoates), Table VII.
- (h) Normal alkyl caprylates (octanoates), Table VIII.
- (i) Normal alkyl pelargonates (nonanoates), Table IX.
- (j) Normal alkyl caprates (decanoates), Table X.
- (k) Normal alkyl laurates (dodecanoates), Table XI.
- (l) Normal alkyl myristates (tetradecanoates), Table XII.
- (m) Normal alkyl palmitates (hexadecanoates), Table XIII.
- (n) Normal alkyl stearates (octadecanoates), Table XIV.
- (o) Normal alkyl arachidates (eicosanoates), Table XV.

The names underlined above and given in the first column of the Tables are those recommended by the BSI in Reference 1. The other names are in general the most widely used of other synonyms. The names marked by an asterisk (*) in the Tables are the names approved by the International Union of Pure and Applied Chemistry (IUPAC).

The Tables also give the molecular weights and the empirical and structural formulae. The Molecular Weights have been calculated from the atomic weights given in Item No.68043.

Experimental values of normal melting and normal boiling points are available for less than half the compounds considered and only a few determinations of the critical temperatures and critical pressures have been made. The method of correlating these data and estimating the values given in the Tables is outlined in Section 4. Values in italics denote that no experimental data were available. It should be noted that for some compounds the normal boiling point and/or critical temperature so derived may be above the decomposition temperature. However, hypothetical values at these temperatures are sometimes necessary for calculating the properties of solutions.

Section 5 refers to three recommended methods which may be used to estimate boiling points at any particular pressure and which require data from this Item only.

It is anticipated that a similar Item for branched chain alkyl esters of normal and branched chain monobasic alkanolic acids will be issued.

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2. NOTATION

P_{br}	reduced pressure of normal boiling point, i.e. $1/P'_c$	
P_c	critical pressure	10^5 N/m^2
P'_c	critical pressure, $(0.9869 P_c)$	atm.
T	temperature	K
T_b	normal boiling point, $(t_b + 273.2)$	K
T_{br}	reduced temperature of normal boiling point, i.e. $\frac{t_b + 273}{t_c + 273}$	
T_c	critical temperature, $(t_c + 273)$	K
t	temperature	$^{\circ}\text{C}$
t_b	normal boiling point	$^{\circ}\text{C}$
t_c	critical temperature	$^{\circ}\text{C}$

3. CONVERSION FACTORS

$$\begin{aligned} \text{Temperature in degrees Fahrenheit} &= \frac{9}{5}t + 32 \\ \text{Temperature in degrees Rankine} &= \frac{9}{5}T \\ 10^5 \text{ N/m}^2 &= 1 \text{ bar} \\ &= 14.5038 \text{ lbf/in}^2 \\ &= 1.0197 \text{ kgf/cm}^2 \\ &= 0.9869 \text{ Standard Atmosphere} \\ &= 750.062 \text{ mmHg.} \end{aligned}$$

4. DERIVATION OF NORMAL MELTING POINTS, NORMAL BOILING POINTS AND CRITICAL POINTS

The normal melting point and normal boiling point data that are available for the compounds considered have been taken from Derivation 4, and the available critical temperature and critical pressure* data from Derivation 3.

Each ester is a member of two homologous series: one series in which the acid radical is the same (i.e. formates, acetates, propionates etc.) and the other series in which the alkyl radical is the same (i.e. methyl esters, ethyl esters, propyl esters etc.). For each of the above four physical properties the experimental data may be plotted in carpet form so that the value for each compound may be assessed in each of its relevant series. In smoothing and extrapolating these data to derive the values given in the Tables the following assumptions have been made.

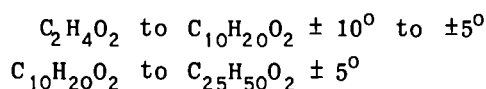
- For each series, the variation of each physical property with carbon number is a smooth function as is the case for the parent alkanes.
- For an infinite chain length the esters and their parent alkanes have the same normal melting point, the same normal boiling point and the same critical point since the structural differences between the esters and their parent alkanes become negligible as the chain length tends to infinity.
- Between isomers there is a smooth variation of the physical property considered.

* It may be noticed that there is some discrepancy between the values of critical pressure selected in Derivation 3 and those in this Item. This is because a comparison of the experimental results of various authors, for liquids other than those considered herein, suggests that the selected values of Derivation 3 are probably slightly low.

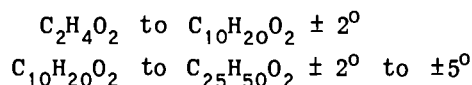


The above procedure enables a self consistent set of data to be obtained for the complete range of compounds considered although the overall accuracy may be expected to vary. The user should therefore allow for some uncertainty in values of the temperatures and critical pressures given in the Tables as detailed below:-

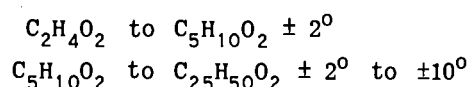
(a) normal melting points,



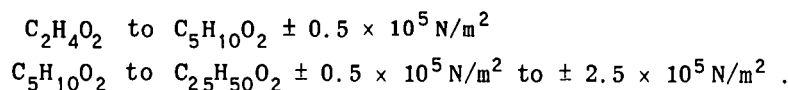
(b) normal boiling points,



(c) critical temperatures,



(d) critical pressures,



Should data for intermediate compounds not given in the Tables, e.g. margarates (heptadecanoates), be required they may be found by interpolation between the corresponding compounds on either side. For example the critical temperature of ethyl margarate is 511°C - the mean of 500°C for ethyl palmitate and 522°C for ethyl stearate. For compounds beyond the range included, the Engineering Sciences Data Unit may be consulted.

5. VAPOUR PRESSURES

For the determination of boiling points at other than atmospheric pressure, the user is referred to one of the following recommended methods given in Chapter 4 of Reference 2.

(a) Riedel Vapour Pressure Correlation.

(b) Frost-Kalkwarf-Thodos Vapour Pressure Correlation.

(c) Riedel-Plank-Miller Vapour Pressure Correlation.

These methods are in the form of reduced equations which require only T_b , T_c and P_c as input data.

6. REFERENCES AND DERIVATION

References

1. - Recommended names for chemicals used in industry. British Standards Institution, B.S. 2474: 1965.
2. REID, R.C.
SHERWOOD, T.K. *The properties of liquids and gases. (Their correlation and estimation.)* 2nd edition. McGraw-Hill Book Company, 1966.

Derivation

3. KUDCHADKER, A.P.
ALANI, G.H.
ZWOLINSKI, B.J. The critical constants of organic substances. *Chem. Rev.*, Vol.68, pp.659-735, 1969.
4. - *Handbook of Chemistry and Physics*, 50th edition, 1969-70. The Chemical Rubber Company, Cleveland, Ohio, USA.

TABLE I

n-Alkyl Formates

(*Methanoic Acid n-Alkyl Esters)

NAMES		CHEMICAL FORMULAE		MOLECULAR WEIGHT	NORMAL MELTING POINT	NORMAL BOILING POINT				CRITICAL POINT		
Recommended (Reference 1)	Synonym	Structural	Empirical			t_b	T_b	T_{br}	P_{br}	t_c	T_c	P_c
						°C	°C	K			°C	K
METHYL FORMATE	METHYL METHANOATE	HCOOCH ₃	C ₂ H ₄ O ₂	60.05	-99	31.5	304.7	0.626	0.0167	214	487	60.8
ETHYL FORMATE	ETHYL METHANOATE	HCOOCH ₂ CH ₃	C ₃ H ₆ O ₂	74.08	-81	54.5	327.7	0.646	0.0211	235	508	47.9
PROPYL FORMATE	PROPYL METHANOATE	HCOO(CH ₂) ₂ CH ₃	C ₄ H ₈ O ₂	88.11	-93	81.3	354.5	0.659	0.0247	264	537	41.0
BUTYL FORMATE	BUTYL METHANOATE	HCOO(CH ₂) ₃ CH ₃	C ₅ H ₁₀ O ₂	102.13	-92	107.5	380.7	0.677	0.0285	290	563	35.6
PENTYL FORMATE	PENTYL METHANOATE	HCOO(CH ₂) ₄ CH ₃	C ₆ H ₁₂ O ₂	116.16	-74	132.2	405.4	0.689	0.0324	315	588	31.4
HEXYL FORMATE	HEXYL METHANOATE	HCOO(CH ₂) ₅ CH ₃	C ₇ H ₁₄ O ₂	130.19	-63	155.7	428.9	0.702	0.0362	338	611	28.0
HEPTYL FORMATE	HEPTYL METHANOATE	HCOO(CH ₂) ₆ CH ₃	C ₈ H ₁₆ O ₂	144.22	-52	178.0	451.2	0.714	0.0403	359	632	25.1
OCTYL FORMATE	OCTYL METHANOATE	HCOO(CH ₂) ₇ CH ₃	C ₉ H ₁₈ O ₂	158.24	-39	199.0	472.2	0.724	0.0444	379	652	22.8
NONYL FORMATE	NONYL METHANOATE	HCOO(CH ₂) ₈ CH ₃	C ₁₀ H ₂₀ O ₂	172.27	-32	218.8	492.0	0.734	0.0485	397	670	20.9
DECYL FORMATE	DECYL METHANOATE	HCOO(CH ₂) ₉ CH ₃	C ₁₁ H ₂₂ O ₂	186.30	-19	238	511	0.744	0.0529	414	687	19.2
UNDECYL FORMATE	UNDECYL METHANOATE	HCOO(CH ₂) ₁₀ CH ₃	C ₁₂ H ₂₄ O ₂	200.32	-12	255	528	0.751	0.0571	430	703	17.7
DODECYL FORMATE	DODECYL METHANOATE	HCOO(CH ₂) ₁₁ CH ₃	C ₁₃ H ₂₆ O ₂	214.35	0	272	545	0.759	0.0614	445	718	16.5
TRIDECYL FORMATE	TRIDECYL METHANOATE	HCOO(CH ₂) ₁₂ CH ₃	C ₁₄ H ₂₈ O ₂	228.38	5	288	561	0.766	0.0658	459	732	15.4
TETRADECYL FORMATE	TETRADECYL METHANOATE	HCOO(CH ₂) ₁₃ CH ₃	C ₁₅ H ₃₀ O ₂	242.40	15	303	576	0.773	0.0699	472	745	14.5
PENTADECYL FORMATE	PENTADECYL METHANOATE	HCOO(CH ₂) ₁₄ CH ₃	C ₁₆ H ₃₂ O ₂	256.43	18	317	590	0.778	0.0741	485	758	13.7
HEXADECYL FORMATE	HEXADECYL METHANOATE	HCOO(CH ₂) ₁₅ CH ₃	C ₁₇ H ₃₄ O ₂	270.46	26	331	604	0.784	0.0781	497	770	13.0
HEPTADECYL FORMATE	HEPTADECYL METHANOATE	HCOO(CH ₂) ₁₆ CH ₃	C ₁₈ H ₃₆ O ₂	284.49	29	344	617	0.790	0.0826	508	781	12.3
OCTADECYL FORMATE	OCTADECYL METHANOATE	HCOO(CH ₂) ₁₇ CH ₃	C ₁₉ H ₃₈ O ₂	298.51	35	356	629	0.795	0.0870	518	791	11.7
NONADECYL FORMATE	NONADECYL METHANOATE	HCOO(CH ₂) ₁₈ CH ₃	C ₂₀ H ₄₀ O ₂	312.54	40	368	641	0.800	0.0909	528	801	11.1
EICOSYL FORMATE	EICOSYL METHANOATE	HCOO(CH ₂) ₁₉ CH ₃	C ₂₁ H ₄₂ O ₂	326.57	44	379	652	0.804	0.0952	538	811	10.6