BOILING POINTS AND DENSITIES OF ACETATES OF NORMAL ALIPHATIC ALCOHOLS

By Mieczysław Wojciechowski [1] and Edgar R. Smith

ABSTRACT

The boiling points, rates of change of boiling point with pressure, and densities
of methyl acetate, ethyl acetate, n-propyl acetate, and n-butyl acetate were
measured by precise comparative methods using water as the reference standard.
As in previous work on the normal saturated hydrocarbons and normal aliphatic
alcohols, it was found that the introduction of each CH_2 group into the chain of a
molecule containing a normal alkyl group of more than some small number n of
carbon atoms causes dt/dp to increase by a constant value which is independent of
the chemical nature of the molecule.

CONTENTS

I. METHODS OF MEASUREMENT

In previous papers it was shown that in the homologous series of
normal saturated hydrocarbons [11] [2] and normal aliphatic alcohols
[12], containing more than some small number n of carbon atoms, the
addition of a CH_2 group to the normal alkyl group to form the next
higher normal alkyl group results in an increase of 0.0029° C per
millimeter of mercury in the coefficient dt/dp at the normal boiling
point. Since this value was found to be independent of the chemical
nature of the compound, the additivity of the effect of the CH_2 group
on dt/dp was postulated. In this paper a similar investigation of the
relation between the dt/dp coefficient and the molecular weight of the
compound in the series of acetates of normal aliphatic alcohols is
described. In addition, there are reported the boiling points and
densities of the following esters: methyl acetate, ethyl acetate, n-
propyl acetate, and n-butyl acetate. For determining boiling points
Świętosławski's ebulliometric technic [7] and comparative method
with water as a primary standard was applied. Details of the experi-
mental procedure for determining the boiling point and the coefficient

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[1] Guest Worker from the Polytechnic Institute, Warsaw, Poland.
[2] The figures in brackets refer to references listed at the end of the paper.

dt/dp have been described briefly in the paper on hydrocarbons [11]. Temperatures were measured with a platinum-resistance thermometer having a coiled filament [4], calibrated at this Bureau and furnished by C. H. Meyers. Normal boiling points were calculated by the use of the formula previously reported [11],

$$t_s = t_s' + \frac{\Delta t_s}{\Delta t_w}(100 - t_w'),$$

where t_s represents the normal boiling point of the substance under investigation, t'_s the boiling point actually measured, and t'_w the boiling point of water actually measured under the same pressure as that of the substance. The ratio $\Delta t_s/\Delta t_w$ at 1 atmosphere was computed from boiling points of the substance and of water under the same pressure, slightly above and slightly below 1 atmosphere.

For the density measurements, the differential method of twin picnometers [5], with water as a reference liquid, was used. To control the purity of substances investigated, Świętosławski's ebulliometric test of purity and his scale for classification of the preparations were used.

II. METHOD OF EXTRAPOLATION OF THE DATA

To compute the physico-chemical constants of the pure compounds a method of extrapolation which has been reported previously [13] was used. The method is similar to that of Świętosławski [7] and is based on the correlation of the data for a given property with the purity of the preparation expressed by Δt, the difference between its boiling point and condensation temperature. This difference is a function of the nature and concentration of the impurities in a substance and is zero if the substance is pure.

Having made the measurements of Δt and of a given physico-chemical constant for a series of preparations of the same compound having different purities, as, for example, a few successive fractions of the distillate from an efficient column, one may plot Δt, the difference between the boiling point and temperature of condensation of each of the preparations, in a differential ebulliometer, against the data obtained for the given constant. Direct extrapolation of the curve to the point where Δt equals zero gives the constant corresponding to the pure substance or azeotropic mixture. If only one impurity is present, Δt is a very nearly linear function of its concentration, and so is the value of any property measured. Hence the relation between Δt and the given property is also very close to linearity. When there are several impurities, which generally is the case, and their concentration is different in each fraction of the distillate, Δt, as well as the property measured, is expressed by a curve whose slope and curvature depend on the nature and concentrations of the impurities. In general, the relation between Δt and the property measured may be expressed by a curve. However, as the degree of purity of the substance investigated becomes higher, the curvature decreases, and for preparations whose purity is such that Δt is only a few thousandths of 1 degree, it becomes nearly linear, thus permitting a reliable extrapolation to $\Delta t = 0$.

III. PURIFICATION OF MATERIALS

The best grades of substances that could be purchased were purified by distillation through an efficient 40-bulb column of the Świętosławski type. Esters are difficult to maintain in a state of high purity, because they are very hygroscopic and readily hydrolyze on boiling. Preparations for the determination of boiling point and related properties were distilled directly into the ebulliometer to avoid contact with moist air. Only fractions distilling at constant temperature, as an evidence of their purity, were taken for measurement. A minute amount of water in the ebulliometer, mostly as water adsorbed on glass, may have slightly contaminated the preparations, but its effect was not differentiated from the effects of traces of other impurities.

1. METHYL ACETATE

Three liters of the best available methyl acetate, reagent grade, was distilled, and only the middle fraction, which distilled practically at constant temperature, was collected. The preparation thus obtained was of the fourth degree of purity on Świętosławski's scale, having Δt equal to $0.014°$ C.

2. ETHYL ACETATE

A preparation of the fifth degree of purity, having $\Delta t = 0.003$, was obtained, but during the determination of its boiling point Δt increased to $0.007°$ C. To calculate the true normal boiling point of ethyl acetate it was assumed that the initial difference Δt, as well as the increase of Δt to $0.007°$ C, was caused by water. To measure the change of boiling point corresponding to such an increase of Δt when caused by water, a small amount of a freshly prepared solution of water in ethyl acetate of the same purity was added to that in the ebulliometer. In this way the correction of boiling point for impurity was determined experimentally.

3. n-PROPYL ACETATE

The middle fraction of the distillate was of high purity, characterized by a Δt of $0.004°$ C.

4. n-BUTYL ACETATE

Distillation through the column yielded two preparations of the fourth degree of purity expressed by $\Delta t = 0.007°$ and $0.015°$ C.

IV. EXPERIMENTAL RESULTS AND CONCLUSIONS

The data obtained for the boiling points of four acetates of normal aliphatic alcohols are given in table 1.

TABLE 1.—*Boiling point data for four esters*

Substance	Δt	Normal boiling point	Normal boiling point extrapolated
	°C	°C	°C
Methyl acetate	0.014	56.32₈	
Ethyl acetate	.003	77.11₂	77.11₄
n-Propyl acetate	.004	101.54₈	
n-Butyl acetate {	.007	126.10₂	126.09₄
	.015	126.11₄	

Table 2 contains the values of dt_s/dt_w, the ratio of change of boiling point of each substance to the change of the boiling point of water caused by a small increment of pressure, and values of dt/dp, the increment of boiling point per millimeter of change of pressure. The values in parentheses were obtained by interpolation.

TABLE 2.—*Data for dt/dp coefficients for four esters*

Substance	$\dfrac{dt_s}{dt_w}$	Boiling point of water	$\left(\dfrac{dt}{dp}\right)_{p=760}$	Difference
		°C	°C/mmHg	
Methyl acetate {	1.0095 (1.0084) 1.0066	101.201 100.000 98.216	} 0.0373	
				0.0028
Ethyl acetate {	1.0856 (1.0849) 1.0837	101.207 100.000 97.853	} .0401	
				.0029
n-Propyl acetate {	1.1678 (1.1642) 1.1567	100.910 100.000 97.932	} .0430	
				.0026
n-Butyl acetate {	1.2356 (1.2346) 1.2296	100.517 100.000 97.511	} .0456	

The data for dt_s/dt_w permit one to calculate the correction for normal boiling points of the substances, within the pressures expressed by the reported boiling points of water. They may serve also to compute the value of dt/dp corresponding to any pressure within the reported limits, by the use of the equation

$$^3\left(\frac{dt}{dp}\right)_s = \frac{dt_s}{dt_w} \cdot \left(\frac{dt}{dp}\right)_w$$

Data for the densities of the esters investigated are given in table 3.

[3] $(dt/dp)_w/=0.03685°/mm.$ L. B. Smith, F. G. Keyes, and H. T. Gerry, Proc. Am. Acad. Arts Sci. 69, 137 (1934); N. S. Osborne and C. H. Meyers, J. Research NBS 13, 1 (1934) RP691.

TABLE 3.—*Data for densities of the esters at 25° C*

Substance	Δt	Density	Average	Density extra-polated
	°C	g/ml	g/ml	g/ml
Methyl acetate	0.014	0.92741 / .92722	0.927 ₂	0.927 ₂
Ethyl acetate	.003	.89464 / .89471	.89468	.8946 ₆
n-Propyl acetate	.004 / .011	.88297 / [1] .88286 [2] .88286	.88297 / .88286	.8830 ₂
n-Butyl acetate	.007 / .015	.87632 / .87627	.87632 / .87627	.8763 ₆

Table 4 contains a comparison of the authors' data with some previously reported.

TABLE 4.—*Comparison of the data of the present work with results reported in the literature*

Substance	Author	Boiling point	$\left(\dfrac{dt}{dp}\right)_{p=760}$	d^{25}_4
Methyl acetate	E. Beckmann and P. Fuchs [2]	57.4	0.0376	--------
	S. Young and G. L. Thomas [14]	57.1	----------	--------
	S. Young [15]	57.1	----------	--------
	J. H. Mathews [3]	57.0 to 57.2	----------	--------
	M. Wojciechowski and E. R. Smith	56.32	.0373	0.927 ₂
Ethyl acetate	S. Young and G. L. Thomas [14]	77.15	.0380	--------
	E. Beckmann and P. Fuchs [2]	76.5	.0468	--------
	J. Timmermans [8]	77.15	----------	--------
	J. Timmermans and Hennaut-Roland [9]	77.15	----------	.89453
	C. P. Smyth and W. S. Wails [6]	76.7 to 76.9	----------	.8943
	J. H. Mathews [3]	77.06	----------	--------
	M. Wojciechowski and E. R. Smith	77.11	.0401	.8946 ₈
n-Propyl acetate	S. Young and G. L. Thomas [14]	101.55	.0440	--------
	E Aries [1]	101.7	----------	--------
	J. H. Mathews [3]	101.35 to 101.6	----------	--------
	M. Wojciechowski and E. R. Smith	101.55	.0430	.8830 ₁
n-Butyl acetate	E. R. Washburn and C. H. Shildneck [10]	125.8	.08	.8769
	M. Wojciechowski and E. R. Smith	126.09	.0456	.8763 ₆

From table 2 it is obvious that in the case of acetates the introduction of each CH_2 group into the chain of a molecule causes an increase of the dt/dp coefficient by a substantially constant value, the average for the esters investigated being equal to 0.0028. This increment agrees with that measured for a series of normal saturated hydrocarbons [11] and normal aliphatic alcohols [12].

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WASHINGTON, January 18, 1937.

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