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EBULLIOMETRIC AND TONOMETRIC STUDY OF NORMAL ALIPHATIC ALCOHOLS

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ABSTRACT

The following normal aliphatic alcohols: methanol, ethanol, *n*-propanol, *n*-butanol, and *n*-amyl alcohol, were prepared in a state of high purity. By the use of Świętoslawski's ebulliometric technique, and the comparative method of measurements using water as a reference liquid, their normal boiling points and coefficients of increase of boiling point with increase of pressure, $\frac{dt}{dp}$, expressed in degrees centigrade per millimeter of mercury, were determined. The following numerical data were obtained: methanol—boiling point 64.509° C; $\frac{dt}{dp}=0.0331$; ethanol—boiling point, 78.325° C; $\frac{dt}{dp}=0.0334$; *n*-propanol—boiling point 97.209; $\frac{dt}{dp}=0.0344$; *n*-butanol—boiling point, 117.726; $\frac{dt}{dp}=0.0372$; *n*-amyl alcohol—boiling point, 138.06; $\frac{dt}{dp}=0.0402$. Beginning with *n*-propanol, the introduction of a CH₂ group into the chain of a normal aliphatic alcohol molecule has a specific effect, increasing $\frac{dt}{dp}$ by a constant value of 0.0029—the same amount as in the case of aliphatic hydrocarbons.

The ebulliometric control of purity of the preparations, the use of substances of extreme purity, and the application of the method of comparative measurements ensure the accuracy of the results reported.

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I. INTRODUCTION

In a previous paper [1]², it was shown that in the homologous series of normal saturated hydrocarbons from *n*-pentane to *n*-octane, inclusive, the coefficient of increase of boiling point with pressure,

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² The figures in brackets throughout this paper refer to the numbered references listed at the end of the paper.

$\frac{dt}{dp}$, is a linear function of the molecular weight, and the introduction of a CH_2 group into the chain of the molecule has a specific effect, increasing this coefficient by 0.0029 degree centigrade per millimeter of mercury. In this paper a similar investigation of the relationship between the molecular weights of normal aliphatic alcohols and their respective values of the coefficient $\frac{dt}{dp}$ is described. In addition, there are reported the normal boiling points of the following alcohols: methanol, ethanol, *n*-propanol, *n*-butanol, and *n*-amyl alcohol.

II. METHOD OF MEASUREMENTS

Świętosławski's ebulliometric technic [2] and his comparative method of measurements [3] with water as a reference liquid, briefly described in the paper on hydrocarbons, were employed for the determination of boiling points and the coefficient $\frac{dt}{dp}$.

The sensitive ebulliometric test of purity [4] of substances and the use of preparations of high purity ensure the accuracy of the values reported.

The boiling points were measured with a platinum-resistance thermometer having a coiled filament and potential terminals [5], kindly furnished by C. H. Meyers.

The normal boiling points were calculated by the use of the formula [1]:

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

where t_s represents the normal boiling point of the substance under investigation; t_s' the boiling point actually measured; t_w' the boiling point of water actually measured under the same pressure as that of the substance; and $\frac{dt_s}{dt_w}$ the ratio of the coefficients $\frac{dt}{dp}$.

III. PURIFICATION OF SUBSTANCES

1. METHANOL

Two liters of the best available commercial methanol of reagent grade was distilled in a 40-bulb Świętosławski improved distilling column [6], and three middle fractions of 200 ml each, which distilled in the limits of 0.001°C , were used for the measurements. These preparations were found to have a difference of 0.001 and 0.002°C between the boiling point and condensation temperature in the differential ebulliometer of standardized dimensions, and were accordingly of the highest degree of purity on Świętosławski's scale for characterizing the purity of liquid substances and of azeotropic mixtures.

2. ETHANOL

The best commercial absolute alcohol was dehydrated and purified by azeotropic distillation from an efficient column, using benzene as an azeotropic agent. Two fractions of the middle part of the dis-

tillate, which distilled at constant temperature, were used for the determination of boiling point and $\frac{dt}{dp}$ ratio. Preparations thus obtained were of the fifth (highest) degree of purity on Świętosławski's scale, having a Δt , difference between boiling point and condensation temperature, equal to 0.001°C .

3. *n*-PROPANOL

n-Propanol was purified by azeotropic distillation, using benzene as an azeotropic agent. The middle fraction was of the fourth degree of purity, having $\Delta t = 0.006^\circ \text{C}$. Another azeotropic distillation of a commercial preparation of *n*-propanol also resulted in a product of the fourth degree of purity, having $\Delta t = 0.014^\circ \text{C}$.

4. *n*-BUTANOL

By a simple distillation of a commercial preparation in the 40-bulb column, two preparations of the highest purity, having $\Delta t = 0.001$ and 0.003°C , were obtained.

5. *n*-AMYL ALCOHOL

Commercial *n*-amyl alcohol was distilled in the 40-bulb column. The samples thus obtained were of the fourth and third degree of purity, having Δt equal to 0.020 and 0.024°C .

IV. EXPERIMENTAL RESULTS

The data obtained in the present work for the boiling points of five normal aliphatic alcohols are given in table 1.

To calculate the boiling points of the substances that were not of the fifth degree of purity on Świętosławski's scale, a method of extrapolation [7] previously reported, was used.

Table 2 contains a comparison of the author's data for boiling point and the coefficient, $\frac{dt}{dp}$, of the alcohols investigated, with those previously reported.

TABLE 1.—Normal boiling point data for five normal aliphatic alcohols

Substance	Preparation number	t	Degree of purity	Normal boiling point	Normal boiling point extrapolated
				$^\circ \text{C}$	$^\circ \text{C}$
Methanol.....	{	1	V	64.508	64.50
		2	V	64.509	
		3	V	64.509	
Ethanol.....	{	1	V	78.325	78.32
		2	V	78.325	
<i>n</i> -Propanol.....	1	.006	IV	97.186	97.20
		.014	IV	97.149	
<i>n</i> -Butanol.....	{	1	V	117.726	117.72
		2	V	117.719	
<i>n</i> -Amyl alcohol.....	{	1	IV	137.953	138.0
		2	III	137.924	

TABLE 2.—Comparison of determinations obtained by various observers

Substance	Author	Boiling point	$\left(\frac{dt}{dp}\right)_{p=760}$
		°C	°C/mm Hg
Methanol	G. C. Schmidt [8].....	66.9	0.0350
	A. Doroszewski [41].....	64.53	-----
	A. Doroszewski and J. Poljanski [16].....	64.57	-----
	J. Timmermans and Hennaut-Roland [9].....	64.65	.035
	J. A. V. Butler, D. W. Thomson, and W. H. MacLenan [10].....	64.46	-----
	M. Wojciechowski.....	64.509	.0331
Ethanol	D. Mendelejew [11].....	78.303	-----
	W. Ramsay and S. Young [12].....	78.30	-----
	G. C. Schmidt [8].....	78.3	.0342
	W. Ramsay and J. Shields [13].....	78.3	.0334
	E. Beckmann and P. Fuchs [14].....	78.6	.0346
	W. A. Noyes and R. R. Warfel [15].....	78.33	-----
	A. Doroszewski and J. Poljanski [16].....	78.35	-----
	J. Wade and R. M. Merriman [17].....	78.39	-----
	T. W. Richards and L. B. Coombs [18].....	78.42	-----
	R. F. Brunel, J. L. Crenshaw, and E. Tobin [19].....	78.30	-----
	W. Pratolongo [20].....	78.30	-----
	W. Świątosławski, A. Zmaczynski, and J. Usakiewicz [21].....	78.318 to 78.320	-----
	L. Harris [22].....	78.37	-----
M. Wojciechowski.....	78.325	.0334	
n-Propanol	W. Brühl [23].....	97.3 to 97.5	-----
	W. H. Perkin [24].....	98.0	-----
	W. Ramsay and S. Young [25].....	97.4	-----
	G. C. Schmidt [8].....	96.9	.0350
	H. Landolt and H. Jahn [26].....	96.1	-----
	E. Beckmann and P. Fuchs [14].....	95.7	.0358
	E. H. Loomis [27].....	97.2	-----
	S. Young and E. C. Fortley [28].....	97.19	-----
	J. Holmes and P. J. Lagemann [29].....	97.2 to 97.4	-----
	A. Doroszewski and T. Rozdstwienski [30].....	97.26	-----
	R. F. Brunel, J. L. Crenshaw, and E. Tobin [19].....	97.19	-----
	V. C. G. Trew and G. M. C. Watkins [31].....	96.6 ($p=744$)	-----
	J. A. V. Butler, D. W. Thomson, and N. H. MacLenan [10].....	97.19±0.02	-----
J. Timmermans and Y. Delcourt [32].....	97.15	.38 (10 mm of Hg)	
M. Wojciechowski.....	97.209	.0344	
n-Butanol	G. W. A. Kahlbaum [33].....	117.6	.0350
	A. Doroszewski and Z. Dworzanczyk [34].....	117.1	-----
	R. F. Brunel, J. L. Crenshaw, and E. Tobin [19].....	117.1	-----
	J. Timmermans and F. Martin [35].....	118.0	.037
	C. P. Smyth and W. S. Walls [36].....	117.2 to 117.4	-----
	V. C. G. Trew and G. M. C. Watkins [31].....	117.25	-----
	R. C. Ernst, E. E. Litkenhous, and J. W. Spanger [37].....	117.69	-----
n-Amyl alcohol	J. A. V. Butler, D. W. Thomson, and W. H. MacLenan [10].....	117.71	-----
	T. J. Webb and C. H. Lindsley [38].....	118.0	-----
	M. Wojciechowski.....	117.726	.0372
	G. Lievens [39].....	137.95	.037
n-Amyl alcohol	T. Timmermans and Hennaut-Roland [40].....	138.25	-----
	J. A. V. Butler, D. W. Thomson, and W. H. MacLenan [10].....	137.60 to 177.70	-----
	M. Wojciechowski.....	138.06	.0402

In table 3 are given the values of $\frac{dt}{dp}$ for the alcohols investigated, and the ratios, $\frac{dt_s}{dt_w}$, of these coefficients to that of water.

TABLE 3.—Data for $\frac{dt}{dp}$ for five normal aliphatic alcohols

Substance	$\frac{dt}{dt_w}$	Boiling point of water	$\left(\frac{dt}{dp}\right)_{p=760}$	Difference between coefficients $\frac{dt}{dp}$
Methanol.....	{ 0.8909 .9073	°C 100.175 97.634	°C/mm Hg 0.0331	0.0003
Ethanol.....	{ .9030 .9035	100.881 98.157	.0334	
<i>n</i> -Propanol.....	{ .9231 .9431	101.043 98.036	.0344	.0010
<i>n</i> -Butanol.....	{ 1.0039 1.0058	100.690 97.201	.0372	.0028
<i>n</i> -Amyl alcohol.....	{ 1.0887 1.0840	101.086	.0402	.0030

V. CONCLUSIONS

The values of the coefficients $\frac{dt}{dp}$ of *n*-amyl alcohol and *n*-propanol are probably slightly affected by impurities in the preparations used in the measurements, but not enough to obscure the specific effect of each CH₂ group introduced into the chain of the alcohol molecule.

From table 3 it is obvious that the increase of $\frac{dt}{dp}$ is not constant up to *n*-propanol. Beginning with *n*-propanol the introduction of each CH₂ group into the chain of the molecule of a normal aliphatic alcohol is accompanied by the same increment in $\frac{dt}{dp}$. The average increment for the alcohols is 0.0029° C. per millimeter of mercury, exactly the same as in the case of the normal aliphatic hydrocarbons. The irregularities observed in the case of alcohols up to *n*-propanol are probably caused by the high degree of association of the molecules of these compounds.

The data previously reported on the normal aliphatic hydrocarbons, together with the data presented in this paper, suggest the following generalization: In any organic molecule containing a normal alkyl group of more than some small number *n* of carbon atoms, the addition of a CH₂ 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 $\frac{dt}{dp}$ at the normal boiling point. The data reported in this paper indicate that for the normal aliphatic alcohols *n*=2, while the data reported in the paper [1] on the normal aliphatic hydrocarbons indicate that for these compounds *n* is not greater than 4. It is possible that $\frac{dt}{dp}$ may be an additive property,

the value of which may be calculated by taking the sum of the values corresponding to all atoms in the molecule of a given compound. Further work is in progress to determine whether this generalization is applicable to other series of compounds.

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