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Vapour pressures and heat capacity measurements on the C_7–C_9 secondary aliphatic alcohols

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Abstract

Molar enthalpies of vaporization of secondary C_7–C_9 alkanols were obtained from the temperature dependence of the vapour pressure measured by the transpiration method. The measured data sets were checked for internal consistency successfully. A large number of the primary experimental results on temperature dependences of vapour pressures of secondary alcohols have been collected from the literature and have been treated uniform in order to derive their vaporization enthalpies at the reference temperature 298.15 K. This collection, together with our experimental results, have helped to ascertain the database for branched aliphatic alcohols.

Keywords: Alcohols; Vapour pressure; Transpiration method; Enthalpy of vaporization; Heat capacity

1. Introduction

The relationship between the structure of organic compounds and their energetics is one of the fundamental problems of contemporary thermochemistry. The quantitative evaluation of substituent effects in terms of enthalpy of formation or enthalpy of vaporization is one of the possible approaches to the general problem of elucidating how the individual parts of a molecule influence each other. In our previous work, we studied in this context linear [1] and branched tertiary alcohols [2,3]. This work continues this line and is concerned with systematic determination of vaporization enthalpies of secondary 2-, 3-, 4-, and 5-alkanols with chain length of seven, eight, and nine atoms. There are only vaporization enthalpies of secondary butanol, pentanol, and hexanol derivatives available in the literature [3–5]. However, these are short chain alcohols and the general question: *is there any enthalpic effect by migration of the hydroxyl group along the alkyl chain* – could be answered only after measurements on the other longer (C_7–C_9) secondary alkanols. Some experimental results on vapour pressures are already available in the literature [4–13]. Two experimental methods, ebulliometric and static, were most frequently used (see table 1). In this work, we applied a transpiration method [1]. Static and transpiration methods work in the temperature ranges close to ambient temperatures. Ebulliometric methods due to high boiling temperatures of alcohols were applied at elevated temperatures (from 320 K up to boiling temperatures). In any case, in order to derive enthalpies of vaporization of alcohols at the reference temperature 298.15 K, the knowledge of the heat capacities are required. These values were measured with help of DSC and applied for the adjusting of experimental results to the reference temperature $T = 298.15$ K.

2. Experimental

2.1. Materials

Samples of secondary aliphatic alcohols were commercially available from Aldrich and Fluka and were further purified by fractional distillation in vacuum. The degree of purity was controlled using a Hewlett–Packard gas

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TABLE 1
Compilation of enthalpies of vaporization of the secondary C_3–C_{16} alkanols

	Technique[a]	Temperature range/K	$\Delta_l^g H_m(T_{av})/(kJ \cdot mol^{-1})$	$C_p^l/(J \cdot mol^{-1} \cdot K^{-1})$	$C_p^g/(J \cdot mol^{-1} \cdot K^{-1})$	$\Delta_l^g H_m/(kJ \cdot mol^{-1})^b$ (298 K)	Reference
2-Propanol	C	298.15				45.2 ± 0.1	[4]
2-Butanol	C	298.15				49.7 ± 0.1	[4]
2-Pentanol	C	298.15				53.0 ± 0.4	[5]
2-Hexanol	T	274.5–309.4	57.8	258.7[5]	158.3	57.0 ± 0.2	[3]
2-Heptanol	E	357.4–423.0	50.7	298.6	181.1	61.5 ± 0.2	[6]
	E	322.9–431.4	51.2			59.9 ± 0.6	[7]
	S	244.0–338.2	62.8			61.5 ± 0.5	[8]
	T	274.9–312.2	62.8			62.1 ± 0.4	This work
2-Octanol	I	283.3–353.2	64.9	326.9	204.3	67.2 ± 0.4	[9]
	E	366.3–480.8	51.2			66.4 ± 0.4	[10]
	S	253.1–353.2	66.0			66.9 ± 0.7	[8]
	T	283.7–329.2	66.9			67.9 ± 0.3	This work
2-Nonanol	S	263.1–363.2	70.8	356.3	226.9	72.0 ± 0.6	[8]
	T	285.7–324.2	72.1			72.9 ± 0.6	This work
2-Decanol	S	278.2–378.3	74.0	386.7[c]	249.8	77.4 ± 0.9	[8]
2-Undecanol	E	344.2–505.0	59.5	417.1[c]	272.7	76.3	[11]
	S	283.3–393.2	75.9			80.8 ± 1.0	[8]
2-Dodecanol	S	293.5–393.1	80.5	447.6[c]	295.6	86.7 ± 1.1	[8]
2-Tetradecanol	S	313.1–428.3	84.0	508.4[c]	341.4	95.4 ± 1.3	[8]
2-Hexadecanol	S	343.3–453.2	86.6	569.2[c]	387.2	103.9 ± 1.3	[8]
3-Pentanol	C	298.15				52.9 ± 0.3	[5]
3-Hexanol	T	278.3–311.5	59.1	286.0[5]	158.3	58.6 ± 0.4	[5]
3-Heptanol	E	325.2–429.8	53.0	294.6[c]	181.1	61.5 ± 0.9	[7]
	E	263.7–294.7	64.6			62.4 ± 0.7	[12]
	S	275.2–311.2	60.7			60.3 ± 0.2	[8]
3-Octanol	I	283.2–353.2	67.0	339.9	204.0	69.3 ± 0.8	[9]
	S	253.2–348.2	66.4			66.2 ± 0.8	[8]
	T	288.3–324.2	66.9			67.9 ± 0.4	This work
3-Nonanol	S	263.1–363.0	69.6	373.6	226.9	71.0 ± 0.8	[8]
	T	263.1–363.0	70.0			70.9 ± 0.3	This work
4-Heptanol	E	320.6–427.4	51.4	306.8	181.1	60.3 ± 0.5	[7]
	E	275.3–311.2	63.2			62.6 ± 0.6	[13]
	T					62.4 ± 0.3	This work
4-Octanol	I	253.2–353.2	64.3	332.1	204.0	66.5 ± 0.7	[9]
	T	288.3–322.3	66.3			67.2 ± 0.5	This work
4-Nonanol	T	285.0–324.2	70.7	367.8	226.9	71.5 ± 0.3	This work
5-Nonanol	T	288.6–334.2	69.4	370.7	226.9	71.4 ± 0.4	This work

[a] Technique: E, ebulliometry; I, Isoteniscopic; T, transpiration; S, static method.
[b] Calculated using vapour pressure data listed in the original work with help of equations (2) and (3).
[c] Value assessed by addition of an appropriate increment [14] C-$(H)_2(C)_2$ to the molar heat capacity of 2-nonanol, measured experimentally in this work.