Determination of Vapor Pressures and Vaporization Enthalpies of the Aliphatic Branched C_5 and C_6 Alcohols

Dmitry Kulikov, Sergey P. Verevkin,* and Andreas Heintz

Department of Physical Chemistry, University of Rostock, Hermannstrasse 14, 18051 Rostock, Germany

The standard molar enthalpies of vaporization $\Delta_l^g H_m^\circ$ of the 14 branched C_5 and C_6 alkanols 2,2-dimethyl-1-propanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, 2-ethyl-1-butanol, 3,3-dimethyl-1-butanol, 2-hexanol, 3-hexanol, 3-methyl-2-pentanol, 4-methyl-2-pentanol, 2-methyl-3-pentanol, 3,3-dimethyl-2-butanol, 2-methyl-2-butanol, 3-methyl-3-pentanol, and 2,3-dimethyl-2-butanol have been determined. The data were obtained from the temperature dependence of the vapor pressure measured by the transpiration method. A linear correlation of enthalpies of vaporization of the secondary alcohols with the number of C atoms has been found. The effect of self-association of aliphatic alcohols in the liquid phase is discussed in terms of the difference of $\Delta_l^g H_m^\circ$(298.15 K) between associating alcohols and their nonassociating alkane homomorphs.

Introduction

Knowledge of vapor pressures and enthalpies of vaporization is indispensable for separation processes and for the assessment of the fate and behavior of environmental contaminants. Experimental data, however, are scarce, especially for the branched members of homologous series of organic compounds. Besides, the available results on vapor pressures and enthalpies of vaporization are not always consistent, as they should be when used for comparison with predictive calculations. Experimental enthalpies of vaporization can be found in the literature.[1−3] In our previous works[4−10] the vaporization enthalpies and vapor pressures of branched alkanes, ethers, esters, carboxylic acids, and olefins were measured by the transpiration method. In a continuation of this research line, the vapor pressures and the standard molar enthalpies of vaporization $\Delta_l^g H_m^\circ$ (298.15 K) of 14 various C_5 and C_6 alkanols divided into three series according to their degree of branching have been studied. *Branched 1-alkanols* include 2,2-dimethyl-1-propanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, 2-ethyl-1-butanol, and 3,3-dimethyl-1-butanol. *Secondary alkanols* comprise 2-hexanol, 3-hexanol, 3-methyl-2-pentanol, 4-methyl-2-pentanol, 2-methyl-3-pentanol, and 3,3-dimethyl-2-butanol. *Tertiary alkanols* studied were 2-methyl-2-butanol, 3-methyl-3-pentanol, and 2,3-dimethyl-2-butanol. We have used these new experimental results together with data already available from the literature[1−3] for correlating the enthalpies of vaporization of alcohols with the number of C atoms and for studying the effect of self-association of aliphatic alcohols in the liquid phase using the differences of $\Delta_l^g H_m^\circ$ (298.15 K) between the associating alcohols and their nonassociating alkane homomorphs.

Experimental Section

Materials. All samples of alcohols were purchased. The degree of purity was controlled with a Hewlett-Packard gas chromatograph (GC) 5890 series II equipped with a flame ionization detector and a Hewlett-Packard 3390A integrator. The carrier gas (nitrogen) flow was 12.1 $cm^3 \cdot s^{-1}$. A capillary column HP-5 (stationary phase cross-linked 5% phenyl methyl silicone) was used with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 μm. The standard temperature program of the GC was $T = 333$ K for 180 s followed by a heating rate of 0.167 $K \cdot s^{-1}$ to $T = 523$ K. The purities of all samples were >0.995 mole fraction. Special care was taken to remove traces of water from the samples by flashing them with nitrogen before using.

Measurements of the Enthalpies of Vaporization Using the Transpiration Method. The enthalpies of vaporization of alcohols were determined by using the method of transference in a saturated stream of nitrogen. The method has been described before[6−9,11] and has proved to give results in excellent agreement with other established techniques for determining vapor pressures of pure substances and enthalpies of vaporization from the temperature dependence of the vapor pressure. About 0.5 g of the sample was mixed with glass beads and placed in a thermostated U-tube of 20 cm length and 0.5 cm diameter. A nitrogen stream was passed through the U-tube at constant temperature (±0.1 K), and the transported amount of material was condensed in a cooled trap. The mass of condensed product was determined by GC analysis using an internal standard (hydrocarbons). The flow rate of the nitrogen stream was measured using a soap bubble flow meter and optimized to reach the saturation equilibrium of the transporting gas at each temperature under study. On the one hand, the flow rate of the nitrogen stream in the saturation tube should be not too slow in order to avoid the transport of material from U-tube due to diffusion. On the other hand, the flow should not be so fast that the stream of nitrogen does not become saturated with the compound under study. We tested our apparatus at different flow rates of the carrier gas to check the lower boundary of the flow rate below which the contribution of the vapor condensed in the trap by diffusion becomes comparable to the transpired one. In our apparatus the contribution due to diffusion was negligible at a flow rate

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* Author to whom correspondence should be addressed (e-mail sergey.verevkin@chemie.uni-rostock.de).

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Table 1. Experimental Results from Measurements of the Vapor Pressure p Obtained by the Transpiration Method

T	m	$V(N_2)$	p	$(p_{\mathrm{exptl}} - p_{\mathrm{calcd}})$	$\Delta_l^g H_m^\circ$	T	m	$V(N_2)$	p	$(p_{\mathrm{exptl}} - p_{\mathrm{calcd}})$	$\Delta_l^g H_m^\circ$
K[a]	mg[b]	dm^3[c]	Pa[d]	Pa	$kJ \cdot mol^{-1}$	K[a]	mg[b]	dm^3[c]	Pa[d]	Pa	$kJ \cdot mol^{-1}$
2-Methyl-2-butanol											
$\ln(p/\mathrm{Pa}) = \frac{352.907}{R} - \frac{85941.183}{R(T/\mathrm{K})} - \frac{115.6}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
274.3	9.63	0.763	374.8	1.8	54.23	288.5	10.20	0.253	1152.0	−29.4	52.59
276.2	7.01	0.482	429.1	−10.0	54.01	291.4	27.70	0.539	1464.0	−4.4	52.26
276.4	21.40	1.380	456.1	9.5	53.99	291.5	13.10	0.253	1475.0	−4.4	52.24
279.2	6.79	0.357	554.5	−10.4	53.67	294.4	22.30	0.337	1876.0	47.9	51.91
279.3	22.60	1.180	559.6	−10.0	53.65	294.5	16.50	0.253	1852.0	10.7	51.90
282.3	26.10	1.030	731.1	3.6	53.31	297.5	20.50	0.253	2298.0	19.6	51.55
282.4	7.44	0.288	745.9	12.5	53.30	300.4	14.80	0.153	2742.0	−42.3	51.21
285.3	27.20	0.842	929.2	6.1	52.96	306.4	22.30	0.153	4112.0	−36.9	50.52
285.4	8.36	0.253	948.4	18.1	52.95						
3-Methyl-2-butanol											
$\ln(p/\mathrm{Pa}) = \frac{343.745}{R} - \frac{84512.196}{R(T/\mathrm{K})} - \frac{110.5}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
280.3	7.59	0.598	367.9	2.6	53.54	292.4	8.93	0.272	933.5	−0.6	52.20
283.3	7.46	0.464	463.1	−2.4	53.21	295.4	8.90	0.218	1159.0	−1.9	51.87
286.3	8.43	0.409	590.5	1.1	52.88	298.4	11.10	0.218	1443.0	8.5	51.54
289.4	8.50	0.327	741.5	−5.6	52.53	301.4	11.90	0.191	1763.0	0.2	51.21
2,2-Dimethyl-1-propanol											
$\ln(p/\mathrm{Pa}) = \frac{281.728}{R} - \frac{66455.012}{R(T/\mathrm{K})} - \frac{37.3}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
274.2	3.56	0.608	171.5	5.7	56.23	292.3	6.84	0.252	770.0	13.4	55.55
277.2	2.92	0.404	210.6	−5.8	56.12	295.3	8.63	0.252	969.3	15.2	55.44
280.2	2.98	0.304	282.3	1.5	56.00	297.5	9.69	0.245	1119.0	−8.3	55.36
281.3	12.10	1.176	296.0	−12.5	55.96	298.3	8.47	0.198	1210.0	12.9	55.33
282.3	3.00	0.247	347.9	12.2	55.93	300.5	12.60	0.257	1388.0	−21.3	55.25
285.3	13.50	0.932	414.6	−16.6	55.81	301.3	8.01	0.149	1518.0	23.5	55.22
285.4	3.81	0.247	440.1	5.3	55.81	303.5	16.90	0.278	1720.0	−33.1	55.13
286.2	4.23	0.252	478.3	14.0	55.78	306.5	17.80	0.233	2150.0	−20.7	55.02
288.5	12.60	0.670	536.0	−23.7	55.69	308.3	13.30	0.149	2506.0	43.9	54.96
289.2	5.34	0.252	602.9	10.9	55.67	311.5	26.50	0.247	3025.0	−43.0	54.84
291.5	7.28	0.294	702.7	−7.8	55.58	312.3	17.40	0.149	3290.0	51.0	54.81
2-Hexanol											
$\ln(p/\mathrm{Pa}) = \frac{342.926}{R} - \frac{88254.695}{R(T/\mathrm{K})} - \frac{100.4}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
274.5	3.14	2.206	35.83	0.18	60.69	294.4	3.66	0.435	205.4	−3.6	58.70
276.5	2.85	1.677	42.47	−0.72	60.49	297.4	3.33	0.310	261.6	−4.4	58.40
279.5	3.49	1.490	58.04	0.79	60.19	300.4	4.27	0.310	335.1	−1.5	58.09
282.5	3.70	1.181	77.23	1.91	59.89	303.4	4.33	0.249	423.3	−0.1	57.79
285.5	3.82	0.961	97.68	−0.72	59.59	306.4	4.09	0.186	533.0	3.5	57.49
288.4	3.96	0.776	125.1	−1.5	59.30	309.4	5.13	0.186	668.2	9.6	57.19
291.4	3.77	0.559	164.8	1.6	59.00						
3-Hexanol											
$\ln(p/\mathrm{Pa}) = \frac{373.466}{R} - \frac{96635.046}{R(T/\mathrm{K})} - \frac{127.7}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
278.3	3.54	1.317	66.86	−0.71	61.10	296.3	3.31	0.247	326.5	0.2	58.80
281.3	4.00	1.094	90.35	0.88	60.71	299.3	4.30	0.247	423.5	9.4	58.41
284.3	4.33	0.894	119.0	1.4	60.33	305.4	4.02	0.149	656.5	−3.3	57.64
287.4	4.15	0.671	151.5	−3.2	59.93	308.4	5.04	0.149	821.4	−0.8	57.25
290.3	4.07	0.498	200.0	1.4	59.56	311.5	6.26	0.149	1020.0	−5.9	56.86
293.3	3.62	0.349	253.1	−2.3	59.18						
2-Methyl-1-pentanol											
$\ln(p/\mathrm{Pa}) = \frac{334.142}{R} - \frac{86801.276}{R(T/\mathrm{K})} - \frac{91.8}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
275.1	2.17	2.334	23.26	0.45	61.55	295.3	3.19	0.560	138.8	−1.1	59.69
278.2	2.48	2.009	30.61	−0.16	61.26	298.2	3.06	0.420	177.2	0.1	59.43
280.2	2.95	1.961	37.17	0.01	61.08	301.3	2.93	0.315	226.3	−0.2	59.14
283.2	2.79	1.401	49.01	−0.01	60.80	304.3	2.78	0.233	289.7	4.0	58.87
286.2	3.01	1.168	63.27	−0.96	60.53	307.3	3.47	0.233	361.5	3.1	58.59
289.2	3.11	0.911	83.46	−0.11	60.25	310.3	3.41	0.187	443.3	−3.8	58.32
292.2	2.98	0.678	107.3	−0.7	59.98	313.2	3.46	0.152	553.0	2.1	58.05
3-Methyl-1-pentanol											
$\ln(p/\mathrm{Pa}) = \frac{325.723}{R} - \frac{84902.415}{R(T/\mathrm{K})} - \frac{77.8}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
280.2	2.57	2.297	27.60	0.13	63.10	301.2	3.39	0.463	178.0	0.7	61.47
283.2	2.89	1.956	36.31	−0.27	62.87	304.2	3.21	0.343	227.4	1.7	61.24
286.2	2.88	1.467	48.05	−0.32	62.64	307.2	2.88	0.244	286.2	0.4	61.00
289.2	3.19	1.223	63.71	0.18	62.40	310.3	3.64	0.244	362.5	−0.2	60.76
292.3	3.25	0.953	83.11	−0.50	62.16	313.2	2.72	0.147	449.6	−1.3	60.54
295.3	3.28	0.733	109.0	0.6	61.93	316.2	3.38	0.147	557.7	−4.2	60.30
298.2	3.36	0.587	139.2	0.8	61.70						

Table 1 (Continued)

T	m	$V(N_2)$	p	$(p_{\mathrm{exptl}} - p_{\mathrm{calcd}})$	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}$	T	m	$V(N_2)$	p	$(p_{\mathrm{exptl}} - p_{\mathrm{calcd}})$	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}$
K[a]	mg[b]	dm^3 [c]	Pa[d]	Pa	kJ·mol^{-1}	K[a]	mg[b]	dm^3 [c]	Pa[d]	Pa	kJ·mol^{-1}
3-Methyl-2-pentanol											
$\ln(p/\mathrm{Pa}) = \frac{384.843}{R} - \frac{99693.449}{R(T/\mathrm{K})} - \frac{139.2}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
275.1	5.65	2.443	57.97	0.71	61.40	295.4	6.78	0.477	346.3	−1.2	58.57
278.2	6.47	2.103	76.38	−0.76	60.97	298.2	6.12	0.343	434.7	0.3	58.18
280.2	6.42	1.710	92.79	−0.28	60.69	301.3	5.63	0.244	560.8	8.2	57.75
283.3	6.86	1.370	123.3	−0.3	60.26	304.4	6.97	0.244	694.1	−4.1	57.32
286.3	7.34	1.123	160.4	−1.1	59.84	307.3	6.90	0.196	854.6	−9.3	56.92
289.3	6.93	0.807	210.2	0.8	59.42	310.3	6.52	0.147	1076.0	5.4	56.50
292.3	6.52	0.587	271.1	1.5	59.01						
4-Methyl-2-pentanol											
$\ln(p/\mathrm{Pa}) = \frac{358.006}{R} - \frac{91499.881}{R(T/\mathrm{K})} - \frac{114.7}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
273.7	2.79	1.239	56.74	0.44	60.11	290.4	3.88	0.386	245.8	−5.3	58.19
275.3	7.92	2.997	66.26	0.64	59.92	293.2	3.98	0.302	321.4	5.5	57.87
278.4	5.74	1.619	88.15	0.39	59.57	296.4	4.19	0.251	407.3	−0.5	57.50
281.4	5.39	1.160	114.9	−0.5	59.22	299.4	4.81	0.227	517.0	2.1	57.16
284.3	4.32	0.725	146.8	−2.4	58.89	301.3	7.95	0.322	600.7	5.8	56.94
287.4	4.57	0.580	193.2	−1.9	58.54						
2-Methyl-3-pentanol											
$\ln(p/\mathrm{Pa}) = \frac{339.411}{R} - \frac{85006.118}{R(T/\mathrm{K})} - \frac{97.4}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
274.9	5.65	1.452	98.3	0.6	58.23	291.4	5.47	0.34	394.2	−11.1	56.62
277.2	5.70	1.211	117.9	−2.7	58.01	293.5	5.14	0.267	470.3	−8.6	56.42
279.4	5.92	1.039	141.9	−5.1	57.79	295.6	5.71	0.241	578.6	14.4	56.21
281.4	6.12	0.848	178.7	3.3	57.60	297.6	6.38	0.241	645.4	−12.4	56.02
283.4	6.71	0.775	213.6	5.0	57.40	304.5	10.90	0.241	1102.0	6.6	55.35
285.4	7.13	0.689	254.9	7.6	57.21	307.5	13.40	0.241	1350.0	−5.0	55.06
287.4	6.43	0.531	297.5	5.1	57.01						
3-Methyl-3-pentanol											
$\ln(p/\mathrm{Pa}) = \frac{382.816}{R} - \frac{97158.369}{R(T/\mathrm{K})} - \frac{139.2}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
275.2	8.11	1.490	137.2	0.0	58.85	291.4	7.25	0.322	551.0	−7.0	56.60
281.4	9.76	0.992	243.6	2.8	57.99	293.4	8.16	0.310	643.1	−11.0	56.32
283.4	9.79	0.843	286.6	−0.1	57.71	297.3	9.10	0.247	899.4	15.2	55.77
285.4	8.60	0.620	341.3	1.0	57.43	299.4	10.70	0.252	1038.0	2.7	55.48
287.4	8.12	0.498	400.6	−1.9	57.15	301.5	11.10	0.222	1212.0	3.3	55.19
289.4	7.20	0.373	473.5	−1.2	56.87						
3,3-Dimethyl-1-butanol											
$\ln(p/\mathrm{Pa}) = \frac{320.639}{R} - \frac{81977.512}{R(T/\mathrm{K})} - \frac{80.6}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
276.2	2.48	1.645	37.70	0.81	59.72	297.3	3.03	0.325	227.4	−0.2	58.02
279.2	3.05	1.540	49.11	0.36	59.47	300.3	3.28	0.280	285.2	−2.4	57.77
282.3	3.35	1.273	64.92	0.37	59.22	303.2	3.09	0.208	360.9	2.2	57.54
285.3	3.87	1.159	82.08	−2.04	58.98	306.3	3.88	0.208	452.8	1.1	57.29
288.2	3.05	0.706	105.8	−2.2	58.75	309.3	3.74	0.161	563.6	2.0	57.05
291.3	3.72	0.648	140.1	0.0	58.50	312.3	5.35	0.185	702.0	7.3	56.81
294.3	3.21	0.439	178.6	−0.5	58.26						
3,3-Dimethyl-2-butanol											
$\ln(p/\mathrm{Pa}) = \frac{330.529}{R} - \frac{81365.459}{R(T/\mathrm{K})} - \frac{92.6}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
279.9	8.07	0.813	247.6	4.3	55.45	300.4	19.20	0.397	1182.0	−21.6	53.55
282.9	9.11	0.714	316.3	3.2	55.17	303.4	21.60	0.357	1473.0	−14.1	53.27
285.7	9.23	0.595	383.2	−10.6	54.91	306.3	24.20	0.317	1856.0	40.7	53.00
288.5	10.20	0.516	485.8	−6.7	54.65	309.3	25.40	0.278	2221.0	0.9	52.72
291.5	11.00	0.434	620.1	−2.2	54.37	312.3	26.60	0.238	2716.0	14.0	52.45
294.4	12.80	0.397	791.6	15.8	54.10	315.3	26.60	0.198	3254.0	−18.9	52.17
297.4	15.80	0.397	971.4	2.4	53.83						
2-Ethyl-1-butanol											
$\ln(p/\mathrm{Pa}) = \frac{342.013}{R} - \frac{89078.896}{R(T/\mathrm{K})} - \frac{96.6}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
275.2	2.18	2.331	23.38	0.4	62.49	298.3	2.47	0.327	183.4	−0.2	60.26
278.3	2.66	2.121	31.03	−0.1	62.20	301.3	2.22	0.232	233.1	−0.6	59.97
283.4	2.48	1.212	50.28	−0.1	61.70	304.3	2.85	0.232	298.0	2.2	59.68
286.4	3.00	1.119	65.63	−0.6	61.41	307.3	3.04	0.198	372.5	0.3	59.39
289.3	3.17	0.909	85.27	−0.5	61.13	310.3	3.60	0.187	467.2	1.5	59.10
292.3	3.08	0.677	111.1	−0.1	60.84	313.3	3.36	0.140	581.8	2.1	58.81
295.4	2.47	0.419	143.6	−1.0	60.54						

[a] Temperature of saturation. N_2 gas flow (0.56−0.82) cm^3·s^{-1}. [b] Mass of transferred sample condensed at $T = 243$ K. [c] Volume of nitrogen used to transfer mass m of sample. [d] Vapor pressure at temperature T calculated from m and the residual vapor pressure at $T = 243$ K.

Table 2. Compilation of Data of Enthalpies of Vaporization $\Delta_l^g H_m^\circ$ (298.15 K) for C_5 Alkanols

	technique^a	C_p(l)^b (298 K)	C_p(g)^b (298 K)	$\Delta C_p{}^c$ (298 K)	$\Delta_l^g H_m^\circ$ (298 K)	ref
		$J\cdot mol^{-1}\cdot K^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$	$kJ\cdot mol^{-1}$	
1-pentanol	C	209.0	132.9	76.1	56.9 ± 0.2^e	16
	E				57.7 ± 1.1	36
2-pentanol	E	228.3	135.4	92.9	54.2	1
	C				53.0 ± 0.4^e	17
	S				55.15^d	23
3-pentanol	S	240.0	135.4	104.6	53.2 ± 0.1	37
					53.6 ± 1.2	14
	S				55.1^d	23
	C				52.9 ± 0.3^e	17
2-methyl-1-butanol	S	203.0	132.9	70.1	55.5^d	23
	C				54.1 ± 0.3^e	17
3-methyl-1-butanol		209.5	132.9	76.6	55.6	1,32
	C				54.3 ± 0.1^e	17
2-methyl-2-butanol	C	247.3	131.7	115.6	49.2 ± 0.4	17
					50.1	33
					49.8 ± 1.2	14
	E				50.2 ± 0.3	15,37
	T				51.5 ± 0.3^d	this work
3-methyl-2-butanol	C	245.9	135.4	110.5	53.5 ± 0.4	24,38
					51.7 ± 0.6	17
					51.9 ± 1.2	14
	T				51.6 ± 0.3^d	this work
2,2-dimethyl-1-propanol		169.9 (cr)	132.6	37.3	50.2	14
	T				55.3 ± 0.3^f	
					$51.8 \pm 0.3^{d,g}$	this work

[a] Techniques: C, calorimetric method; E, ebulliometry; T, transpiration; S, static method. [b] Molar heat capacity of liquid and gas, respectively, taken from ref 13. [c] Molar heat capacity difference between liquid and gaseous phases. [d] Derived using eqs 5 and 6 with the molar heat capacity difference ΔC_p. [e] Value recommended in ref 24. [f] Compound is solid and its $\Delta_l^g H_m^\circ$ was measured. [g] Enthalpy of vaporization $\Delta_l^g H_m^\circ$ was calculated by subtraction of the enthalpy of fusion[39] $\Delta_{cr}^g H_m^\circ = 3.50\ kJ\cdot mol^{-1}$ from the measured value of $\Delta_{cr}^g H_m^\circ$.

up to $0.11\ cm^3\cdot s^{-1}$. The upper limit of the flow rate at which saturation of the nitrogen stream was achieved in our apparatus was $1.7\ cm^3\cdot s^{-1}$. Thus, we carried out the experiments in the flow rate interval of $(0.56-0.82)\ cm^3\cdot s^{-1}$, which ensured that the transporting gas was in saturated equilibrium with the coexisting liquid phase in the saturation tube. Assuming that Dalton's law of partial pressures of ideal gaseous mixtures applied to the saturated nitrogen stream is valid, values of the vapor pressure p were calculated according to

$$p = mRT_a/V(N_2)M \tag{1}$$

where $R = 8.31451\ J\cdot K^{-1}\cdot mol^{-1}$, m is the mass of transported compound, $V(N_2)$ is the volume of transporting gas, M is the molar mass of the compound, and T_a is the soap bubble meter temperature. The volume of the gas $V(N_2)$ transferred through the tube was determined from the flow rate and time measurements. The flow rate was maintained constant with help of the high-precision needle valve (Hoke). The accuracy of the volume $V(N_2)$ measurements from the flow rate was assessed to be $\pm 0.001\ dm^3$.

The vapor pressure p at each saturation temperature was calculated from the mass of sample collected within a definite time period. The thermodynamic relation for the equilibrium existing between the vapor and the liquid phase of a pure substance is

$$\frac{dp}{dT} = \frac{\Delta_l^g H_m^\circ}{T\Delta_l^g V_m} \tag{2}$$

where $\Delta_l^g V_m$ is the molar volume difference between the vapor phase and the liquid phase. At low pressure the volume of the liquid phase may be neglected in comparison with that of the vapor, and in the case of nonassociating or weakly associating vapors at sufficiently low pressures, the ideal gas law may be adopted, neglecting contributions arising from the second virial coefficients. The result is the Clausius−Clapeyron equation:

$$-\frac{R\cdot d\ln(p)}{d(1/T)} = \Delta_l^g H_m^\circ \tag{3}$$

Under the assumption that

$$\begin{cases} \Delta_l^g H_m^\circ \cong \Delta_l^g H_{m,T_0}^\circ + \Delta C_p(T - T_0) \\ \Delta_l^g V_m \cong \dfrac{RT}{p} \end{cases} \tag{4}$$

which may be justified at sufficiently low vapor pressures, eq 3 is integrated and the temperature dependence of the vapor pressure is described by the equation

$$R\ln(p) = a + (b/T) + \Delta C_p \ln(T/T_0) \tag{5}$$

which is fitted to the experimental p,T data using a and b as adjustable parameters. The following equation gives the value of the vaporization enthalpy at temperature T:

$$\Delta_l^g H_m^\circ(T) = -b + \Delta C_p T \tag{6}$$

$\Delta C_p = C_p(l) - C_p(g)$ is the difference of the molar heat capacities of the liquid and gaseous phases, respectively. T_0 appearing in eqs 4 and 5 is an arbitrarily chosen reference temperature. The molar enthalpies of vaporization $\Delta_l^g H_m^\circ$ have been calculated as a function of temperature using eq 6. These values together with the coefficients a and b according to eq 5 are listed in Table 1. Values of ΔC_p are based on experimental results for the molar heat capacity $C_p(l)$ measurements of alkanols,[12,13] and values of $C_p(g)$ were calculated according to the procedure developed by Domalski.[13] These values are compiled in Tables 2 and 3. The experimental results of the enthalpies of vaporization $\Delta_l^g H_m^\circ$ or sublimation $\Delta_{cr}^g H_m^\circ$ are listed in Tables 2

Table 3. Compilation of Data of Enthalpies of Vaporization $\Delta_l^g H_m^\circ$ (298.15 K) for C_6 Alkanols

	technique[a]	$C_p(l)$[b] (298 K) $J \cdot mol^{-1} \cdot K^{-1}$	$C_p(g)$[b] (298 K) $J \cdot mol^{-1} \cdot K^{-1}$	ΔC_p[c] (298 K) $J \cdot mol^{-1} \cdot K^{-1}$	$\Delta_l^g H_m^\circ$ (298 K) $kJ \cdot mol^{-1}$	ref
1-hexanol	C				61.6 ± 0.2[e]	16
	C	242.5	155.8	86.7	61.9 ± 0.2	25
	T				61.1 ± 0.2	8
2-hexanol					54.8	14
	S	258.7	158.3	100.4	56.96[d]	26
	E				57.9 ± 0.2	29
	T				58.3 ± 0.3[d]	this work
3-hexanol	E				58.5 ± 1.2	15,30
	S	286.0	158.3	127.7	58.3[d]	23
	S				55.1[d]	26
	S				57.0 ± 0.2	31
	T				58.6 ± 0.4[d]	this work
2-methyl-1-pentanol					55.6	14
	S	247.6	155.8	91.8	63.4[d]	23
	T				59.4 ± 0.3[d]	this work
3-methyl-1-pentanol					62.3	14
	T	233.6	155.8	77.8	61.7 ± 0.3	this work
4-methyl-1-pentanol					60.5	1,32
		272.3	155.8	116.5	67.8	14
2-methyl-2-pentanol	E	289.0	154.6	134.4	54.8[e]	33
					59.8	14
3-methyl-2-pentanol	S				58.4[d]	23
		293.8	154.6	139.2	56.9	14
	T				58.2 ± 0.3[d]	this work
4-methyl-2-pentanol	S				58.0[d]	23
		273.0	158.3	114.7	50.6	14
	T				57.3 ± 0.3	this work
2-methyl-3-pentanol					54.4	14
	E	255.7	158.3	97.4	56.7 ± 0.1	29
	T				56.0 ± 0.5[d]	this work
3-methyl-3-pentanol	E				56.7 ± 0.9	34
	T	293.8	154.6	139.2	55.7 ± 0.3[d]	this work
2,2-dimethyl-1-butanol		228.4	155.5	72.9	56.1	14
3,3-dimethyl-1-butanol	C	236.1	155.5	80.6	61.01	35
	T				58.0 ± 0.2[d]	this work
2,3-dimethyl-2-butanol	E	277.5	157.3	120.2	54.0 ± 0.8	34
3,3-dimethyl-2-butanol	T	250.6	158.0	92.6	53.8 ± 0.3[d]	this work
2-ethyl-1-butanol	S				63.5[d]	23
		252.8	156.2	96.6	63.2	14
	T				60.3 ± 0.3[d]	this work

[a] Techniques: E, ebulliometry; T, transpiration; S, static method. [b] Molar heat capacity of liquid and gas, respectively, taken from ref 13. [c] Molar heat capacity difference between liquid and gaseous phases. [d] Derived using eqs 5 and 6 with the molar heat capacity difference ΔC_p. [e] Value recommended in ref 24.

and 3. The error in the enthalpies of vaporization is assumed to be accurate within ± 0.3 kJ·mol^{-1}.

Results and Discussion

Enthalpies of Vaporization from the Transpiration Method. Data for the vapor pressures and enthalpies of vaporization of C_5 and C_6 alcohols have been published by a number of groups (see Tables 2 and 3). A critical survey of these values up to 1973 was reported by Wilhoit and Zwolinski.[14] Then, Majer and Svoboda[1] reviewed their own data and literature data on enthalpies of vaporization available until 1984. Recently Roganov and Baranov[15] gathered literature data on enthalpies of vaporization of alcohols and especially experimental results published in the difficult to obtain sources from the former USSR. We have used these compilations as well as the recent original papers for a survey of enthalpies of vaporization of C_5 and C_6 alcohols as listed in Tables 2 and 3. Only calorimetrically measured enthalpies of vaporization at 298.15 K have been reported by Wadsö[16] and McCurdy and Laidler.[17] Hovorka and co-workers[18−22] made vapor−pressure measurements of a number C_6 alcohols. Vapor−pressure measurements were also reported by Thomas et al.[23] for several aliphatic C_5 and C_6 alcohols over a wide range of temperature. Comparison of the vapor pressures reported by these authors with our results is presented in Figures 1−9.

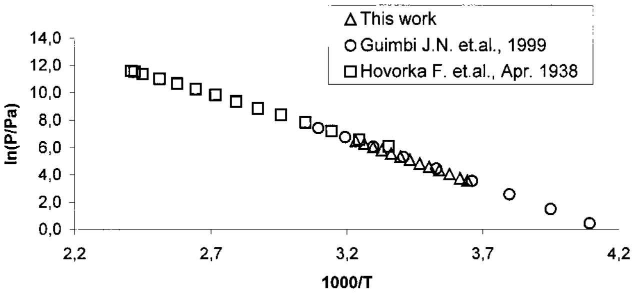

Figure 1. Vapor pressure data for 2-hexanol.

The vapor pressures measured in this work are not always in agreement with those from the literature. The discrepancy could be explained with the ill-defined purity of the compounds used by some of the previous investigators[18−22] because methods of analysis at the time of their works were not as refined as are now available. In other cases our values are in much better agreement with those found in the literature. Therefore, we did not consider Hovorka's data, and only Thomas's[23] and N'Guimby's[26] data have been treated by using eq 5 and 6 in order to derive enthalpies of vaporization at 298.15 K. Comparison of values of $\Delta_l^g H_m^\circ$ (298.15 K) obtained from literature data assumed to be reliable is shown in Tables 2 and 3. For

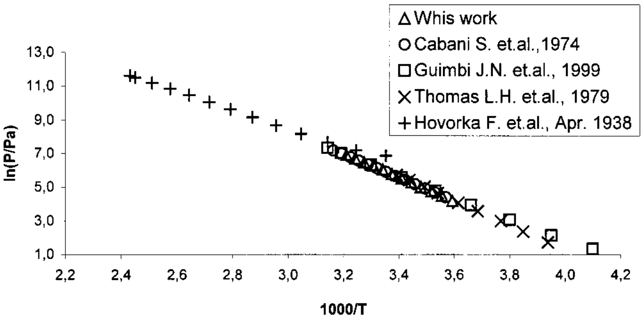

Figure 2. Vapor pressure data for 3-hexanol.

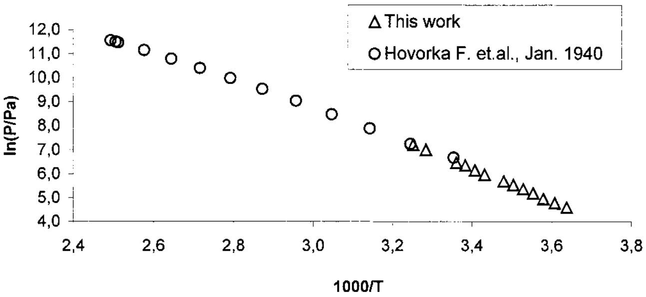

Figure 3. Vapor pressure data for 2-methyl-3-pentanol.

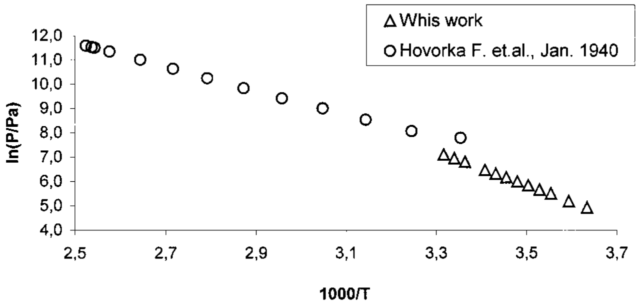

Figure 4. Vapor pressure data for 3-methyl-3-pentanol.

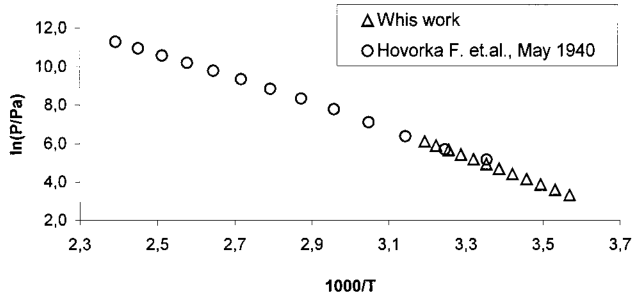

Figure 5. Vapor pressure data for 3-methyl-1-pentanol.

further discussion values of $\Delta_l^g H_m^\circ$ (298.15 K) selected by Pedley[24] as well as our own results have been chosen together with values for linear alcohols taken from the literature (see Table 4).

Correlation of $\Delta_l^g H_m^\circ$ of Secondary Alcohols with the Number of C Atoms. The correlation of the enthalpies of vaporization with the number of C atoms of the alcohols is a valuable method to study the systematic behavior of homologous series. The vaporization enthalpy $\Delta_l^g H_m^\circ$ appears to be a linear function of the number of carbon atoms in homologous series of alkanes, alcohols, halogenoalkanes, and aliphatic esters according to results measured by Mansson, Sellers et al.[25] We have used values of $\Delta_l^g H_m^\circ$ (298.15 K) available from the literature[24,26] for 2-alkanols and 3-alkanols with chain lengths of C_3-C_{16} to test how our results for 2-hexanol and 3-hexanol fit into systematic dependence on the chain length. It can be seen from Figure 10 that our data for both isomers fit very well in the linear correlation specific for each type of branching. The following empirical equations for the enthalpy of vaporization could be obtained using the experimental data[24,26] presented in Figure 10:

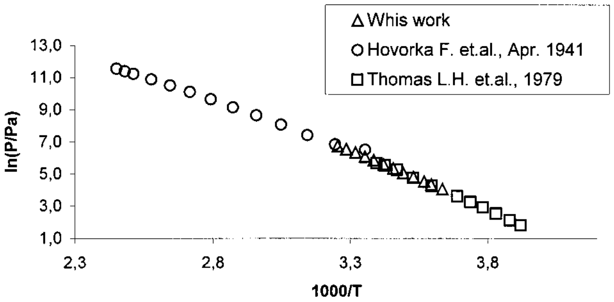

Figure 6. Vapor pressure data for 3-methyl-2-pentanol.

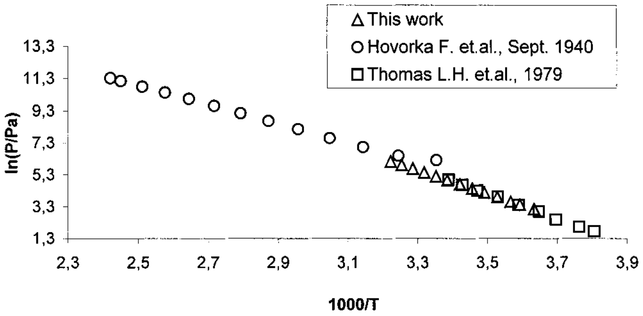

Figure 7. Vapor pressure data for 2-ethyl-1-butanol.

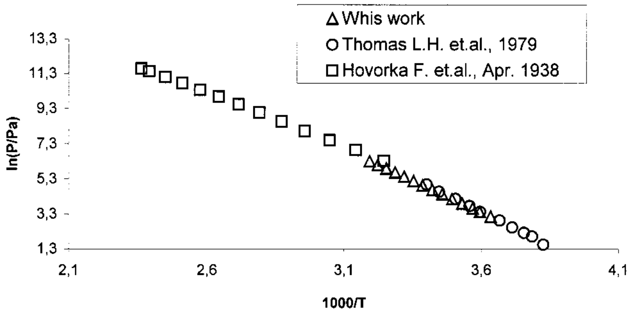

Figure 8. Vapor pressure data for 2-methyl-1-pentanol.

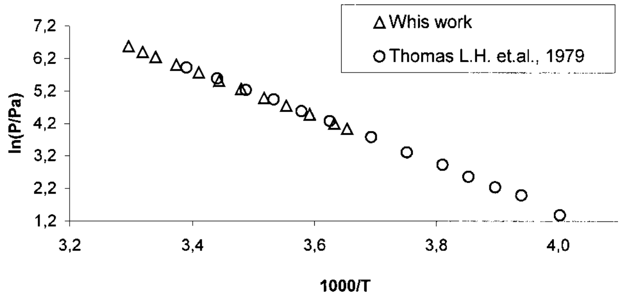

Figure 9. Vapor pressure for 4-methyl-2-pentanol.

for 2-alkanols:

$$\Delta_l^g H_m^\circ \text{ (298.15 K)/(kJ·mol}^{-1}) = 30.60 + 4.66N \quad (7)$$

for 3-alkanols:

$$\Delta_l^g H_m^\circ \text{ (298.15 K)/(kJ·mol}^{-1}) = 33.71 + 4.09N \quad (8)$$

N is the number of C atoms in the alkanol.

Association of Aliphatic Alcohols in the Liquid Phase. The enthalpy of vaporization of alcohols can provide

Table 4. Association of Aliphatic Alcohols in the Liquid Phase at 298.15 K (See Text)

	R	$\Delta_l^g H_m^\circ$(exptl) ROH kJ·mol^{-1}	$\Delta_l^g H_m^{\circ\,a}$ RCH$_3$ kJ·mol^{-1}	$\Delta(\Delta_l^g H_m^\circ)$ ROH−RCH$_3$ kJ·mol^{-1}
		Linear 1-Alkanols		
1-pentanol	C_5H_{11}	57.0 ± 0.2[a]	31.6	25.4
1-hexanol	C_6H_{13}	61.1 ± 0.3[b]	36.5	24.6
1-heptanol	C_7H_{15}	66.8 ± 0.2[a]	41.5	25.3
1-octanol	C_8H_{17}	70.1 ± 0.3[b]	46.5	23.6
1-nonanol	C_9H_{19}	76.9 ± 0.2[a]	51.4	25.5
1-decanol	$C_{10}H_{21}$	80.9 ± 0.3[b]	56.3	24.6
1-undecanol	$C_{11}H_{23}$	84.7 ± 0.3[b]	61.2	23.5
1-dodecanol	$C_{12}H_{25}$	90.0 ± 0.3[b]	66.4	23.6
1-tridecanol	$C_{13}H_{27}$	95.8 ± 0.6[b]	71.3	24.5
1-tertadecanol	$C_{14}H_{29}$	98.7 ± 0.6[b]	76.1	22.6
1-pentadecanol	$C_{15}H_{31}$	102.5 ± 0.3[b]	81.4	21.1
1-hexadecanol	$C_{16}H_{33}$	108.8 ± 0.7[b]	86.0	22.8
		Branched 1-Alkanols		
2-methyl-1-propanol	C_4H_9	50.8 ± 0.1[a]	25.2	25.6
2-methyl-1-butanol	C_5H_{11}	54.1 ± 0.3[c]	30.3	23.8
3-methyl-1-butanol	C_5H_{11}	54.3 ± 0.1[c]	29.8	24.5
2,2-dimethyl-1-propanol	C_5H_{11}	51.9 ± 0.3[b]	27.7	24.2
4-methyl-1-pentanol	C_6H_{13}	60.5[c]	34.9	25.6
2-methyl-1-pentanol	C_6H_{13}	59.4 ± 0.2[b]	34.9	24.5
3-methyl-1-pentanol	C_6H_{13}	61.7 ± 0.2[b]	35.1	26.6
2-ethyl-1-butanol	C_6H_{13}	60.3 ± 0.1[b]	35.2	25.1
2,2-dimethyl-1-butanol	C_6H_{13}	56.1[c]	32.4	23.4
3,3-dimethyl-1-butanol	C_6H_{13}	58.0 ± 0.2[b]	32.4	25.6
		Linear Secondary Alkanols		
2-propanol	C_3H_7	45.3 ± 0.2[a]	20.0	25.3
2-butanol	C_4H_9	49.7 ± 0.2[a]	25.2	24.5
2-pentanol	C_5H_{11}	53.0 ± 0.4[c]	29.8	23.2
3-pentanol	C_5H_{11}	52.9 ± 0.3[c]	30.3	22.6
2-hexanol	C_6H_{13}	58.3 ± 0.2[b]	34.9	23.4
3-hexanol	C_6H_{13}	58.7 ± 0.4[b]	35.1	23.6
		Branched Secondary Alkanols		
3-methyl-2-butanol	C_5H_{11}	51.6 ± 0.1[b]	29.1	22.5
3-methyl-2-pentanol	C_6H_{13}	58.2 ± 0.2[b]	34.2	24.0
4-methyl-2-pentanol	C_6H_{13}	57.3 ± 0.2[b]	32.9	24.4
2-methyl-3-pentanol	C_6H_{13}	56.0 ± 0.5[b]	34.2	21.8
3,3-dimethyl-2-butanol	C_6H_{13}	53.8 ± 0.3[b]	32.0	21.8
		Tertiary Alkanols		
2-methyl-2-propanol	C_4H_9	46.7 ± 0.1[a]	22.4	24.3
2-methyl-2-butanol	C_5H_{11}	51.5 ± 0.4[b]	27.7	23.8
2-methyl-2-pentanol	C_6H_{13}	54.8 ± 0.1[c]	32.4	22.4
3-methyl-3-pentanol	C_6H_{13}	55.7 ± 0.3[b]	33.0	22.7
2,3-dimethyl-2-butanol	C_6H_{13}	54.0 ± 0.8[c]	32.0	22.0

[a] Result from Pedley et al.[24] [b] Result from our previous work.[8] [c] Values selected from Tables 2 and 3.

information on molecular association.[27,28] To define the association effects, the difference of $\Delta_l^g H_m^\circ$ (298.15 K) between an alcohol and its alkane homomorph is considered. The latter is a substance having a molecular size and structure very similar to those of the studied alcohol, but which does not associate. The simplest approach is to replace a hydroxyl group by a methyl group. It is assumed[27] that the nonassociative intermolecular energy between the two compounds is very similar and has a negligible effect on the change in the properties compared to the effect of association. Then the difference between the enthalpies of vaporization of the associating substance (ROH) and its homomorph (RCH_3) is a measure of the intermolecular energy due to the association in the liquid phase. As the degree of association in alcohols is much greater in the liquid than in the vapor, the difference in the $\Delta_l^g H_m^\circ$ (298.15 K) between homomorphs reflects primarily association in the liquid phase.

In Table 4 the experimental enthalpies of vaporization $\Delta_l^g H_m^\circ$ (298.15 K) of a number of alkanols (ROH) including linear ones are listed together with the corresponding values of the homomorph alkanes (RCH_3). A remarkable constancy for the differences $\Delta(\Delta_l^g H_m^\circ)$ of 22−25 kJ·mol^{-1} is observed being not significantly dependent on the kind and branching of the C atoms number of the alcohols. This nearly constant value could serve as a crude measure of association caused by hydrogen bonding in pure liquids. Values of $\Delta(\Delta_l^g H_m^\circ)$ correspond approximately to the enthalpy of the formation of hydrogen bonds per mole of alcohol. No significant relationship between $\Delta(\Delta_l^g H_m^\circ)$ and the structure of alcohols is observed. This fact suggests that the variation of the degree of association caused by the alkyl substituents is small.

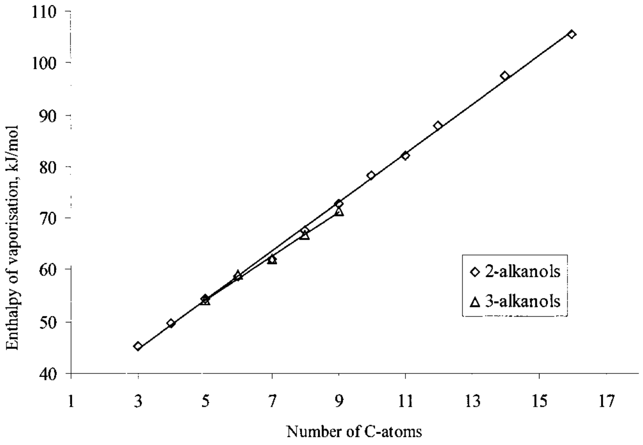

Figure 10. Correlation of enthalpies of vaporization $\Delta_l^g H_m^\circ$ (298.15 K) with the number of C atoms in 2- and 3-alkanols. Experimental values for $\Delta_l^g H_m^\circ$ (298.15 K) of 2-propanol, 2-butanol, 2-pentanol, 2-hexanol, and 3-hexanol were taken from Table 4. Values of $\Delta_l^g H_m^\circ$ (298.15 K) for 2-heptanol, 61.5 kJ·mol^{-1}; 3-heptanol, 61.5 kJ·mol^{-1}; 2-octanol, 66.9 kJ·mol^{-1}; 3-octanol, 66.2 kJ·mol^{-1}; 2-nonanol, 72.1 kJ·mol^{-1}; 3-nonanol, 70.9 kJ·mol^{-1}; 2-decanol, 77.6 kJ·mol^{-1}; 2-undecanol, 8.14 kJ·mol^{-1}; 2-dodecanol, 87.2 kJ·mol^{-1}; 2-tetradecanol, 96.8 kJ·mol^{-1}; and 2-hexadecanol, 104.8 kJ·mol^{-1}, were calculated by treatment of the experimental $p-T$ measurements from ref 26 using eqs 5 and 6.

Literature Cited

(1) Majer, V.; Svoboda, V. *Enthalpies of Vaporization of Organic Compounds*; IUPAC Chemistry Data Series 32; Blackwell Scientific Publications: London, U.K., 1985.

(2) Chickos J. S. Heats of Sublimation. In *Molecular Structure and Energetics, Physical Measurements*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1987; Vol. 2, Chapter 2, pp 67−150.

(3) Lebedev, Yu. A.; Miroshnichenko, E. A. *Thermochemistry of Organic Substance Evaporation in Thermochemistry and Equilibria of Organic Compounds*; Frenkel, M., Ed.; VCH Publishers: New York, 1993.

(4) Verevkin, S. P.; Beckhaus, H.-D.; Belen'kaja, R. S.; Rakus, K.; Rüchardt, C. Geminal Substituent Effects. 9. Enthalpies of Formation and Strain Free Increments of Branched Esters and Ethers. *Thermochim. Acta* **1996**, *279*, 47−64.

(5) Verevkin, S. P.; Heintz, A. Determination of Vaporization Enthalpies of the Branched Esters from Correlation Gas-Chromatography and Transpiration Methods. *J. Chem. Eng. Data* **1999**, *44*, 1240−1245.

(6) Verevkin, S. P. Measurement and Prediction of Monocarboxylic Acids Thermochemical Properties. *J. Chem. Eng. Data* **2000**, *45*, 946−952.

(7) Verevkin, S. P.; Wandschneider, D.; Heintz, A. Determination of Vaporization Enthalpies of Selected Linear and Branched C_7, C_8, C_9, C_{11}, and C_{12} Monoolefin Hydrocarbons from Transpiration and Correlation Gas-Chromatography Methods. *J. Chem. Eng. Data* **2000**, *45*, 618−625.

(8) Kulikov, D.; Verevkin, S. P.; Heintz, A. Enthalpies of vaporization of a series of linear aliphatic alcohols. Experimental results and predicted values using the ERAS-model. *Fluid Phase Equilib.* **2001**, submitted for publication.

(9) Chickos, J. S.; Hesse, D. G.; Hosseini, S.; Liebman, J. F.; Mendenhall, G. D.; Verevkin, S. P.; Rakus, K.; Beckhaus, H.-D.; Rüchardt, C. Enthalpies of Vaporisation of Some Highly Branched Hydrocarbons. *J. Chem. Thermodyn.* **1995**, *27*, 693−705.

(10) Verevkin S. P. Thermochemistry of Alcohols: Experimental Standard Molar Enthalpies of Formation and Strain of Some Alkyl and Phenyl Congested Alcohols. *Struct. Chem.* **1998**, *9*, 375−382.

(11) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: London, U.K., 1970.

(12) Domalski, E. S.; Hearing, E. D. Heat capacities and enthropies of organic compounds in the condensed phase. *J. Phys. Chem. Ref. Data* **1990**, *19*, 881−1047.

(13) Domalski, E. S.; Hearing, E. D. Estimation of the thermodynamic properties of C−H−N−O−S−Halogen compounds at 298.15 K. *J. Phys. Chem. Ref. Data* **1993**, *22*, 805−1159.

(14) Wilhoit, R. C.; Zwolinski B. J. Physical and Thermodynamical Properties of Alcohols. *J. Phys. Chem. Ref. Data* **1973**, *2* (Suppl. 1).

(15) Roganov, G. N.; Baranov, O. M. Additivity of enthalpies of formation and evaporation of mono- and diatomic alcohols. *Vestsi Nats. Akad. Navuk Belarusi, Ser. Khim. Navuk* **1999**, *4*, 49−54.

(16) Wadso, I., A heat of vaporization calorimeter for work at 25 °C and for small amounts of substances. *Acta Chem. Scand.* **1966**, *20*, 536−544.

(17) McCurdy, K. G.; Laidler, K. J. Heats of vaporization of a series of aliphatic alcohols. *Can. J. Chem.* **1963**, *41*, 1867−1871.

(18) Hovorka, F.; Lankelma, H. P.; Stanford, S. C. Thermodynamic Properties of the Hexyl Alcohols. II. Hexanols-1, -2, -3 and 2-Methylpentanol-1 and -4. *J. Am. Chem. Soc.* **1938**, *60*, 820−827.

(19) Hovorka, F.; Lankelma, H. P.; Axelrod, A. E. Thermodynamic Properties of the Hexyl Alcohols. III. 2-Methylpentanol-3 and 3-Methylpentanol-3. *J. Am. Chem. Soc.* **1940**, *62*, 187−189.

(20) Hovorka, F.; Lankelma, H. P.; Axelrod, A. E. Thermodynamic Properties of the Hexyl Alcohols. IV. 3-Methylpentanol-1 and 2-Methylpentanol-5. *J. Am. Chem. Soc.* **1940**, *62*, 1096−1098.

(21) Hovorka, F.; Lankelma, H. P.; Smith, W. R. Thermodynamic Properties of the Hexyl Alcohols. V. 2,2-Dimethylbutanol-1 and 2-Ethylbutanol-1. *J. Am. Chem. Soc.* **1940**, *62*, 2372−2374.

(22) Hovorka, F.; Lankelma, H. P.; Bishop, J. W. Thermodynamic Properties of the Hexyl Alcohols. VI. 2,3-Dimethylbutanol-1 and 3-Methylpentanol-2. *J. Am. Chem. Soc.* **1941**, *63*, 1097−1098.

(23) Thomas, L. H.; Meatyard, R.; Smith, H.; Davies, G. H. Vapor pressure and molar entropies of vaporization of monohydric alcohols. *J. Chem. Eng. Data* **1979**, *24*, 159−161.

(24) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; TRC Data Series; Texas A&M University: College State, TX, 1994; Vol. 1.

(25) Mansson, M.; Sellers, P.; Stridh, G.; Sunner, S. Enthalpies of vaporization of some 1-substituted *n*-alkanes, *J. Chem. Thermodyn.* **1977**, *9*, 91−97.

(26) N'Guimbi, J.; Berro, C.; Mokbel, I.; Rauzy, E.; Jose, J. Experimental vapour pressures of 13 secondary and tertiary alcohols—correlation and prediction by a group contribution method. *Fluid Phase Equilib.* **1999**, *162*, 143−158.

(27) Majer, V.; Svoboda, V.; Pick, J. *Heats of Vaporization of Fluids*; Elsevier: Amsterdam, The Netherlands, 1989.

(28) Benson, S. W. Some observation of the structures of liquid alcohols and their heats of vaporization. *J. Am. Chem. Soc.* **1996**, *118*, 10645−10649.

(29) Brazhnikov, M. M.; Andreevskii, A. I.; Satschek, A. I.; Peschenko, A. D. Vapor pressures of some seocodary alcohols and calculation of their enthalpies of vaporization. *Zh. Prikl. Khim. (Leningrad)* **1975**, *48*, 2181−2185.

(30) Satschek, A. I. Ph.D. Thesis, University of Minsk, Belorussia, 1980.

(31) Cabani, S.; Conti, G.; Mollica, V.; Lepori, L. Thermodynamic study of dilute aqueous solutions of organic compounds. Part 4. Cyclic and straight chain secondary alcohols. *J. Chem. Soc., Faraday Trans. 1 (London)* **1975**, *71*, 1943−1954.

(32) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. *Neutral Thermochemical Data in NIST Standard Reference Database Number 69*; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, Nov 2000; http://webbook.nist.gov.

(33) Majer, V.; Svoboda, V. *Fluid Phase Equilib.* **1985**, *20*, 111−136.

(34) Wiberg, K. B.; Hao, S. Enthalpies of hydration of alkenes. 4. Formation of acyclic *tert*-alcohols. *J. Org. Chem.* **1991**, *56*, 5108−5110.

(35) Ulbig, P.; Klüppel, M.; Sculz, S. Extension of the UNIVAP group contribution method: enthalpies of vaporization of special alcohols in the temperature range from 313 to 358 K. *Thermochim. Acta* **1996**, *271*, 9−12.

(36) Green, J. H. S. Revision of the values of the heats of formation of normal alcohols. *Chem. Ind. (London)* **1960**, 1215−1216.

(37) Peschenko, A. D.; Shvaro, O. V.; Zubkov, V. I. *Thermodyn. Org. Soedin. (Gorky)* **1988**, 39−41.

(38) Connett, J. E., Chemical equilibria. Part III. Dehydrogenation of pentan-1-ol, pentan-2-ol, and 3-methylbutan-2-ol. *J. Chem. Soc. A* **1970**, 1284−1286.

(39) Granzow, B. J. *Mol. Struct.* **1996**, *381*, 127−132.

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