

Platform Chemicals from Ethylene Glycol and Isobutene: Thermodynamics “Pays” for Biomass Valorisation and Acquires “Cashback”

Sergey P. Verevkin ^{1,2,*} and Aleksandra A. Zhabina ³

¹ Competence Centre CALOR, Department Life, Light & Matter of Faculty of Interdisciplinary Research, University of Rostock, 18059 Rostock, Germany

² Department of Physical Chemistry, Kazan Federal University, 420008 Kazan, Russia

³ Chemical Department, Samara State Technical University, 443100 Samara, Russia; aazhab@gmail.com

* Correspondence: sergey.verevkin@uni-rostock.de

Table S1

Auxiliary quantities: formula, density ρ (293 K), massic heat capacity c_p (298.15 K), and expansion coefficients $(\delta V/\delta T)_p$ of the materials used in the present study ^a

Materials	Formula	ρ (293 K)	c_p (298.15 K)	$(\delta V/\delta T)_p$ ^b
		$\text{g}\cdot\text{cm}^{-3}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$	$10^{-3}\cdot\text{cm}^3\cdot\text{K}^{-1}\cdot\text{g}^{-1}$
EGM	$\text{C}_8\text{H}_8\text{O}_2$	0.897 [1]	2.31 ^c	1.0
polyethylene	$\text{CH}_{1.93}$	0.92	2.53	0.1
cotton	$\text{CH}_{1.774}\text{O}_{0.887}$	1.50	1.67	0.1

^a Data for the densities, ρ (293 K), and the specific heat capacities, c_p (298.15 K), of auxiliary materials are from our previous work [2]. The specific energy of combustion $\Delta_c u^0(\text{cotton}) = -16945.2 \text{ J}\cdot\text{g}^{-1}$; $u(\Delta_c u^0) = 4.2 \text{ J}\cdot\text{g}^{-1}$. The specific energy of combustion $\Delta_c u^0(\text{polyethylene}) = -46357.3 \text{ J}\cdot\text{g}^{-1}$; $u(\Delta_c u^0) = 3.6 \text{ J}\cdot\text{g}^{-1}$. The standard uncertainties are reported for the specific energies of combustion.

^b Estimated.

^c Calculated from the molar heat capacity at 298.15 K (see Table S3).

Table S2

Compilation of data on molar heat capacities $C_{p,m}^0(\text{liq})$ and heat capacity differences $\Delta_l^g C_{p,m}^0$ (in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) at $T = 298.15 \text{ K}$

Compounds	$C_{p,m}^0(\text{liq})$ ^a	$-\Delta_l^g C_{p,m}^0$ ^b	$C_{p,m}^0(\text{g})$ ^c
EGM	273.5 [3] 269.2	81.7	191.8
EGD	357.2	103.5	253.7

^a Calculated according to group-additivity procedure developed by Chickos and Acree. [4]

^b Calculated according to empirical procedure developed by Chickos *et al.* [5].

^c Calculated as the sum of column 2 and 3 in this table.

Adjustment of vaporisation/sublimation enthalpies to the reference temperature $T = 298.18$ K

The vaporisation enthalpies, which are derived from the experimental vapor pressure-temperature dependencies according to the Clausius–Clapeyron relation, are referenced to the average temperature, T_{av} , of the examined interval. For engineering calculations, these enthalpies should be adjusted to the reference temperature $T = 298.15$ K. The enthalpies of sublimation/vaporisation are derived using the following equation:

$$\Delta_1^g H_m^o(T) = -b + \Delta_1^g C_{p,m}^o \times T \quad (S1)$$

The $\Delta_1^g C_{p,m}^o$ -values used in Equation (S2) are usually derived according to empirical equations developed by Chickos and Acree [4].

$$\Delta_1^g C_{p,m}^o(298.15 \text{ K}) = -0.26 \times C_{p,m}^o(\text{liq}, 298.15 \text{ K}) - 10.58 \quad (S2)$$

where $C_{p,m}^o(\text{liq}, 298.15 \text{ K})$ values are of experimental origin or they can be also estimated according to the group-additivity procedure [5].

Transpiration method [6-8]

Absolute vapour pressures of EGM were measured using the transpiration method. The details of this method can be found elsewhere. A brief description and the necessary details are compiled here. The main idea of this method is to saturate the gas stream flowing over the sample and to determine the amount of compound transferred by the gas within a given time. Approximately 0.5 to 0.8 g of the sample is mixed with glass beads (diameter 1 mm) and placed in the thermostatted U-shaped saturator. The glass beads are needed to enlarge the contact area between gas and sample. A stream of nitrogen at a well-defined flow rate was passed through the saturator at constant temperature (± 0.1 K), and the transported material was collected in a cold trap. The amount of the condensed substance was determined by GC. The saturation vapour pressure p_i at each temperature T_i was calculated from the amount of condensate collected within a definite period of time:

$$p_i = m_i \cdot R \cdot T_a / V \cdot M_i ; \quad V = (n_{N_2} + n_i) \cdot R \cdot T_a / P_a \quad (S3)$$

where V is the volume of the gas phase consisting of the n_{N_2} moles of the carrier gas and n_i mole of gaseous compound under study (with the molar mass M_i) at the atmospheric pressure P_a and the ambient temperature T_a . The volume of the carrier gas V_{N_2} was determined by the digital flow rate sensor from integration with a microcontroller. We used the Honeywell S&C - HAFBLF0200C2AX5 digital flow rate sensor with uncertainty at the level of 2.5 %. The flow rate of the nitrogen stream was also controlled by using a soap bubble flow meter (HP soap film flowmeter (model 0101-0113)) and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The volume of the carrier gas V_{N_2} was readied from the digital flow rate sensor. The amount of the compound under investigation n_i in the carrier gas was estimated at each temperature using the ideal gas law.

Before starting the vapour pressure measurements, the sample was first pre-conditioned at 310-320 K (within about one hour) in order to remove possible traces of water. The saturator was then kept at 310-315 K (to remove possible traces of volatile compounds). In order to assure the competition of pre-conditioning at the selected temperature, three samples were taken during the sample flashing at and analyzed by the GC. A constant vapour pressure at this temperature indicated that the transpiration experiments could begin. GC analysis of the transported material did not reveal any additional contamination. The absence of impurities and decomposition products was re-checked by GC analysis of the saturator content at the end of the entire series of experiments.

Static Method [9,10]

The vapour pressures of EGM were measured by the static method, using the sample from the same batch as for the transpiration method. The detailed description of the experimental apparatus, procedure, and uncertainty analysis, is given elsewhere [9,10]. The stainless steel cylindrical cell with the sample was kept at a constant temperature within ± 0.02 K. The sample cell was connected to the high temperature capacitance manometers (*MKS Baratron 631B13LBFP* and *MKS Baratron 631C13MBFP*) covering the working range of (0.1 to 10^5) Pa. Standard uncertainties of 0.5 % for the pressure readings for both manometers were stated by the manufacturer. The temperature of tubing connections between the measuring cell and pressure gauges was kept higher by 30-50 K than those in the sample cell in order to avoid condensation of sample in the tubing system. The expanded uncertainty (0.95 confidence level) of absolute temperature determination was 0.05 K

over the working temperature interval of the system. The experimental setup and the measuring procedure were tested in our previous work with measurements on benzoic acid, naphthalene, ferrocene, and benzophenone as the reference compounds [9,10]. Experimental results are given in Table 2.

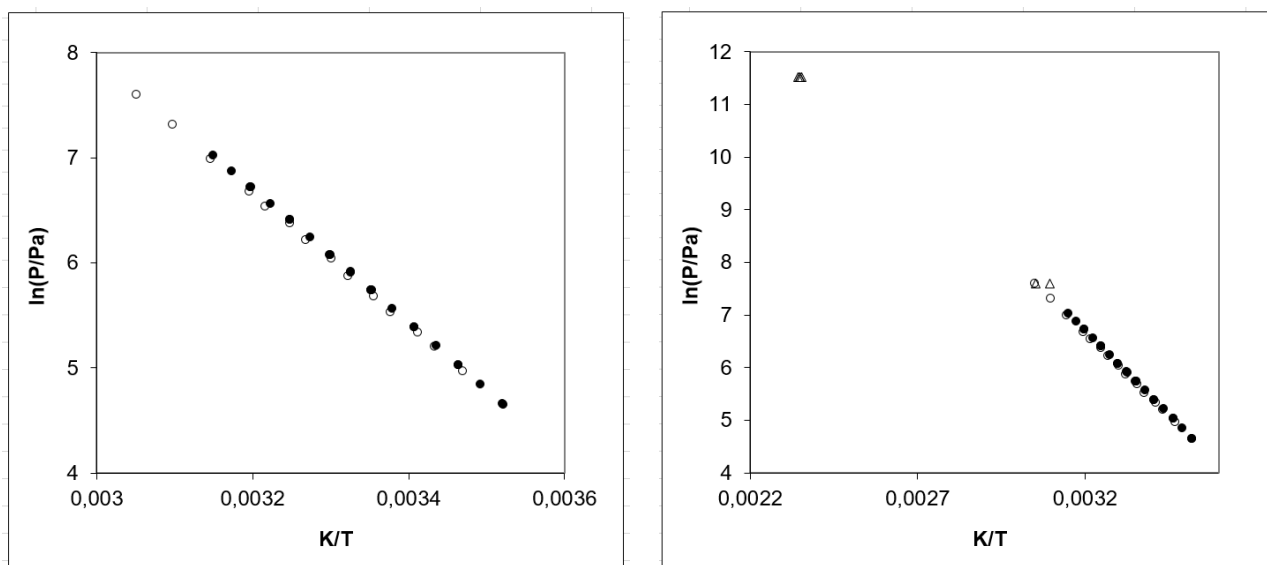


Figure S1. Comparison of vapour pressures measured in this work over the liquid sample of ethylene glycol mono-tert-butyl ether (EGM):

● - transpiration method, this work; ○ - static method, this work; Δ – boiling points at different pressures [11,12].

Table S3

The vapour pressures p , and standard vaporisation enthalpies and entropies obtained by the approximation of boiling points at different pressures available in the literature [11,12].

$T/$ K^a	$p/$ Pa	$\Delta_l^g H_m^o/a$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_l^g S_m^o/$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
ethylene glycol mono-tert-butyl ether (EGM):		$\Delta_l^g H_m^o(298.15\text{ K}) = (50.8\pm 2.2)\text{ kJ}\cdot\text{mol}^{-1}$ $\Delta_l^g S_m^o(298.15\text{ K}) = (124.0\pm 3.1)\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	
$\ln(p/p_{\text{ref}}) = \frac{301.4}{R} - \frac{75181.2}{RT} - \frac{81.7}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1\text{ Pa}$			
323.0	2000	48.8	118.5
327.7	2000	48.4	115.2
425.0	101325	40.5	95.3
426.0	101325	40.4	94.9
426.0	101325	40.4	94.9
427.0	101325	40.3	94.5
ethylene glycol di-tert-butyl ether (EGD):		$\Delta_l^g H_m^o(298.15\text{ K}) = (53.5\pm 1.8)\text{ kJ}\cdot\text{mol}^{-1}$ $\Delta_l^g S_m^o(298.15\text{ K}) = (127.7\pm 1.2)\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	
$\ln(p/p_{\text{ref}}) = \frac{327.0}{R} - \frac{84327.7}{RT} - \frac{103.5}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1\text{ Pa}$			
360.0	6666	47.1	108.2
335.0	2000	49.7	115.7
444.0	101325	38.4	86.5

^a Uncertainty of the vaporisation enthalpy is expressed as the standard uncertainties. They include uncertainties from the fitting equation, and uncertainties from temperature adjustment to $T = 298.15 K$. Uncertainties

in the temperature adjustment of vaporisation enthalpies to the reference temperature $T = 298.15$ K are estimated to account with 20 % to the total adjustment.

Table S4.

Thermochemical data at $T = 298.15$ K ($p^\circ = 0.1$ MPa) for reference compounds (in $\text{kJ}\cdot\text{mol}^{-1}$) [13]

Compounds	$\Delta_f H_m^\circ(\text{liq})$	$\Delta_f^\circ H_m^\circ$	$\Delta_f H_m^\circ(\text{g})_{\text{exp.}}$
isobutene	-37.5 ± 0.9	20.6 ± 0.2	-16.9 ± 0.9
ethylene glycol [14]	-454.9 ± 1.2	66.0 ± 0.2	-388.9 ± 1.2
methanol	-239.1 ± 0.3	37.6 ± 0.2	-201.5 ± 0.3
methyl tert-butyl ether	-313.6 ± 1.1	30.1 ± 0.2	-283.5 ± 1.1

Table S5

Experimental thermodynamic constants of reactions according to Equation (1) and Equation (2) reported by Chang *et al.* [15]

T/K	K_a (1)	K_a (2)
318.2	8.69	13.46
328.2	5.55	8.33
353.2	2.65	3.95
373.2	1.38	1.77
393.2	0.73	0.89
363.2	2.04	2.81
343.2	3.00	5.06
363.2	1.43	2.27
383.2	0.82	1.28
340.2	3.89	5.02
353.2	2.84	4.33

References

1. Evans, T. W.; Edlund, K. R. Tertiary alkyl ethers, preparation and properties. *Ind. Eng. Chem.* **1936**, 28, 1186-1188. doi: 10.1021/ie50322a015
2. 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, 1240-1244. doi:10.1021/je990122a
3. Atake, T.; Kawaji, H.; Tojo, T.; Kawasaki, K.; Ootsuka, Y.; Katou, M.; Koga, Y. Heat Capacities of Isomeric 2-Butoxyethanols from 13 to 300 K: Fusion and Glass Transition. *Bull. Chem. Soc. Japan* **2000**, 73, 1987-1991.
4. Chickos, J.S.; Acree, W.E. Enthalpies of sublimation of organic and organometallic compounds. 1910-2001. *J. Phys. Chem. Ref. Data* **2002**, 31, 537-698. doi: 10.1063/1.1475333
5. Chickos, J.S.; Hosseini, S.; Hesse, D.G.; Liebman, J.F. Heat capacity corrections to a standard state: a comparison of new and some literature methods for organic liquids and solids. *Struct. Chem.* **1993**, 4, 271-278. doi: 10.1007/BF00673701

6. Verevkin, S.P.; Emel'yanenko, V.N. Transpiration method: Vapor pressures and enthalpies of vaporization of some low-boiling esters. *Fluid Phase Equilib.* **2008**, *266*, 64–75. doi:10.1016/j.fluid.2008.02.001
7. Verevkin, S.P.; Sazonova, A.Y.; Emel'yanenko, V.N.; Zaitsau, D.H.; Varfolomeev, M.A.; Solomonov, B.N.; Zherikova, K.V. Thermochemistry of halogen-substituted methylbenzenes. *J. Chem. Eng. Data* **2015**, *60*, 89–103. doi: 10.1021/je500784s
8. Emel'yanenko, V.N.; Verevkin, S.P. Benchmark thermodynamic properties of 1,3-propanediol: Comprehensive experimental and theoretical study. *J. Chem. Thermodyn.* **2015**, *85*, 111–119. doi:10.1016/j.jct.2015.01.014
9. Zaitsau, D. H.; Verevkin, S. P.; Sazonova, A. Y. Vapor pressures and vaporization enthalpies of 5-nonanone, linalool and 6-methyl-5-hepten-2-one. Data evaluation. *Fluid Phase Equilib.* **2015**, *386*, 140–148. doi: 10.1016/j.fluid.2014.11.026
10. Zaitsau, D.H.; Verevkin, S.P. Vapor Pressure of Pure Methyl Oleate—the Main Component of Biodiesel. *Russ. J. Gen. Chem.* **2021**, *91*, 2061–2068. doi:10.1134/S1070363221100236
11. SciFinder—Chemical Abstracts Service. Available online: <https://scifinder.cas.org/> (accessed on 28.03.2023).
12. Reaxys. Available online: <https://www.reaxys.com/> (accessed on 28.03.23).
13. Pedley, J. P.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed. Chapman and Hall: London, UK, 1986.
14. Verevkin, S.P.; Emel'yanenko, V.N.; Nell, G. 1,2-Propanediol. Comprehensive experimental and theoretical study. *J. Chem. Thermodyn.* **2009**, *41*, 1125–1131. doi:10.1016/j.jct.2009.04.019
15. Chang, T.-K.; Hwang, J.-H.; Huang, H.-Y.; Su, W.-B.; Hong, C.-T. The thermodynamics properties for the liquid phase synthesis of ethylene glycol tert-butyl ether and ethylene glycol di-tert-butyl ether. *Shiyou Jikan.* **2012**, *48*, 21–37. CODEN:SYCKE4 ISSN:1022-9671.