J. Chem. Eng. Data **2000,** *45,* 988−990

Articles

Selected Physicochemical Properties of Dibutoxymethane

Marcela Palczewska-Tulińska and Andrzej M. Szafrański*

Industrial Chemistry Research Institute, Physicochemical Laboratory, 8 Rydygiera Street,
01-793 Warsaw, Poland

Liquid densities, viscosities, heat capacities, thermal conductivities, and saturated vapor pressures were measured for 99.98 mol % pure dibutoxymethane over the temperature ranges (293−393) K, (283−403) K, (293−416) K, (283−373) K, and (366−453) K, respectively, by using an Anton Paar densimeter, a Hoepler viscosimeter, a Perkin-Elmer DSC 1B, the “hot wire” technique, and comparative ebulliometry, respectively. The experimental data were correlated and smoothed values or deviations, and for vapor pressure data, overall measures of data reproducibility are given.

Introduction

Chemically, dibutoxymethane [2568−90−3], $CH_2(OC_4H_9)_2$, is an acetal (formaldehyde dibutylacetal or dibutyl formal) and at the same time an ether (methyleneglycol dibutyl ether). It is a dialkyl derivative of aldehyde hydrate and is produced by treating an aldehyde with an alcohol. As a relatively versatile compound, it is used in the manufacture of synthetic resins, antiseptics, deodorants, and fungicides. Acetals including dibutoxymethane have been reported to be useful as fuel additives, improving the octane number of gasolines or the *n*-cetane number of diesel fuels and decreasing smoke and particulate emissions.[1] There are only fragmentary physicochemical property data available for dibutoxymethane. Its liquid and gas enthalpies of formation are (−549.4 ± 1.7) and (−501.3 ± 3.0) $kJ\cdot mol^{-1}$ at 298.15 K, respectively, the heat of evaporation is (48.1 ± 2.5) kJ mol^{-1} at 298.15 K, and the standard enthalpy of combustion is (5850 ± 1.7) $kJ\cdot mol^{-1}$.[2]

The compound is practically insoluble in water, 1 cm^3 in 100 cm^3 water at 293.15 K; it is less dense than water and produces a heteroazeotrope with water (∼62% by mass of water) boiling at 371.25 K.[3] The compound is an important industrial chemical, and it was deemed of interest to measure some property data including saturated vapor pressure, liquid density, viscosity, liquid heat capacity, and liquid thermal conductivity. Generally, there are no comparable data to be found at the comparable conditions of the present study.

Experimental Section

Chemicals. A laboratory substance, 99% pure, was dried for 48 h over 4A molecular sieves and then rectified through a 35-theoretical plate column. A forerun, about 25%, was collected at a reflux ratio of 1:30. The major fraction was collected within the boiling temperature range of ±0.005 K. The resulting product was 99.98 mol % pure. It was found by Fischer’s method to contain 0.02% (by mass) of water. Gas chromatography showed no other contaminants to be present. This product was used for the physicochemical measurements.

Table 1. Experimental Results for Liquid Density, ρ and $\Delta\rho$, of Dibutoxymethane from 293.15 K to 393.15 K

T/K	ρ/$kg\cdot m^{-3}$	$\Delta\rho$/$kg\cdot m^{-3}$	T/K	ρ/$kg\cdot m^{-3}$	$\Delta\rho$/$kg\cdot m^{-3}$
293.15	835.45	0.08	342.15	792.41	−0.02
298.65	830.42	0.16	349.15	785.98	0.22
303.15	826.65	0.00	354.15	781.75	0.02
309.15	821.38	0.02	360.15	776.45	−0.01
313.15	817.92	−0.02	366.15	771.11	0.00
322.45	809.71	0.03	373.15	765.02	−0.14
328.15	804.74	−0.01	378.15	760.43	−0.01
333.15	800.24	0.09	384.15	755.06	0.00
338.15	795.93	0.01	393.15	747.01	−0.01

Results

Density. The literature[4−6] reports only single-temperature data for liquid dibutoxymethane, usually at 293.15 K. The values vary from 831 $kg\cdot m^{-3}$ to 837.5 $kg\cdot m^{-3}$. Vogel’s data [7] (835.4−781.3) $kg\cdot m^{-3}$ at (293.15−359.05) K, identical with the present value at room temperature, are becoming increasingly high as the temperature is increased. Vogel’s material may well have been impure because Vogel’s boiling point is by 0.42 K higher than the present boiling point.

An Anton Paar densimeter DMA 60/DMA 602H was used to measure the density over the temperature range (293.15−393.15) K. The temperature of the measuring cell in the densimeter was controlled with a thermostat with a circulating medium to within ±0.03 K. A precision quartz thermometer was used to read the cell temperature to an accuracy of ±0.015 K. The oscillation period (τ) in the vibrating U-tube of the densimeter was converted to density by using the following equation:

$$\rho = A(\tau^2 - B) \tag{1}$$

where the A and B constants were established by using the literature data for pure water and dry air. The uncertainty in the density measurement was estimated to be ±0.01 $kg\cdot m^{-3}$. Data are listed in Table 1. The experimental values were correlated by the parabolic equation

10.1021/je000070l CCC: $19.00

$$\rho/\mathrm{kg{\cdot}m^{-3}} = 1079.78 - 0.7965T/\mathrm{K} - (1.27027 \times 10^{-4})(T/\mathrm{K})^2 \quad (2)$$

Viscosity. So far no viscosity data have been reported for liquid dibutoxymethane. Viscosities were measured with a Hoeppler viscosimeter over a temperature range of (283.15−403.15) K. The measurements were accurate to within ±0.001 mPa·s. Data are listed in Table 2. The experimental data were correlated with the equation

$$\log(\eta/\mathrm{mPa{\cdot}s}) = -1.85894 + \frac{541.0837}{T/\mathrm{K} - 5.7569} \quad (3)$$

Liquid Heat Capacity. So far no heat capacity data have been reported for liquid dibutoxymethane. The heat capacity of dibutoxymetane was measured over the temperature range (293.15−393.15) K with a DSC-1B Perkin-Elmer differential scanning microcalorimeter. The uncertainty in the liquid heat capacity measurement was estimated to be ±0.01 J mol^{-1} K^{-1}. Sapphire, 99.9999% pure, was used as a standard. The experimental data (Table 3) were correlated by the use of the equation

$$c_\mathrm{p}/\mathrm{J{\cdot}m^{-1}{\cdot}K^{-1}} = 90.23 + 0.8794T/\mathrm{K} - (2.117 \times 10^{-4})(T/\mathrm{K})^2 \quad (4)$$

Thermal Conductivity. The literature contains no data on the thermal conductivity of liquid dibutoxymethane. The measurements were carried out by the most commonly used transient method, the “hot wire” method, which measures the temperature gradient produced when a thin wire of low thermal capacity is heated. The measuring cell was a water-jacketed capillary, which made a double-step precision thermostating possible. A thin platinum wire was placed concentrically inside the capillary, which was placed in a Wheatstone bridge circuit to dermine λ from measurements of the heat source alone. The capillary was filled with liquid dibutoxymethane, electric current was passed at varying intensities, and at each intensity the resistance of the wire was measured. The calibration constants for the measuring cell were evaluated from measurements carried out for water and methyl alcohol as standard liquids. The uncertainty in the thermal conductivity measurement was estimated to be ±0.1 mW·m^{-1}·K^{-1}. The data measured (Table 4) were correlated with the following equation

$$\lambda/\mathrm{mW{\cdot}m^{-1}{\cdot}K^{-1}} = 140.0 - 0.28(T/\mathrm{K} - 273.15) \quad (5)$$

Vapor Pressure. The comparative ebulliometric technique comprising a dynamic twin-ebulliometer assembly was used as described elsewhere.[8] Temperature was measured with a platinum resistance thermometer (Leeds & Northrup, model 8163-C) operated in conjunction with a Mueller bridge (Leeds & Northrup, type G-2) and an electronic null detector (Leeds & Northrup, model 9834). To provide replicate data, each equilibrium point was measured six times. The maximum uncertainty in the temperature measurement and the associated pressure inconstancy were estimated at ±5 mK and ±6.7 Pa, respectively. To obtain the fits to the Antoine equation

$$\ln P/\mathrm{kPa} = 13.2185 - \frac{2975.26}{T/\mathrm{K} - 107.273} \quad (6)$$

the maximum likelihood method was used, as described in more detail elsewhere.[8,9] Table 5 lists the observed (T_i, P_i) data pairs, their estimated precision measures ($\sigma_{T,\mathrm{s}}$, $\sigma_{P,\mathrm{s}}$), and the deviations (ΔT_i, ΔP_i) between the calculated and observed variables. The ΔT_i, ΔP_i values allow us to check whether the values obtained for error variances are appropriate, by assessing whether the variations in these fall properly within their (computed) confidence intervals. Since neither ΔT_i nor ΔP_i alone is adequately representative as an overall measure of reproduction for an individual data point, we suggested[10]

$$\kappa_i^\mathrm{s} = [\mathrm{sgn}(\Delta T_i)]\kappa_i/\hat{\sigma} \quad (7)$$

where, for the present case,

$$\kappa_i = [(\Delta P_i/\sigma_{P_i})^2 + (\Delta T_i/\sigma_{T_i})^2]^{1/2} \quad (8)$$

as an overall measure of data-point reproduction, where κ_i is the distance between the i-th observed and estimated data points in the (P, T) space, and σ_T and σ_P are adopted as length units. The κ_i values are seen (eq 8) to be scaled with respect to $\hat{\sigma}$, that is, to the standard deviation of κ_i.[8] The sign of ΔT_i has been attributed to κ_i to have the experimental point located “below” or “above” the response curve. When systematical errors are absent, κ_i should be randomly distributed about zero; large κ_i values ($\gg$1) may indicate outliers. The κ_i values listed in Table 5 are seen

Table 2. Experimental Results for Liquid Viscosity, η and $\Delta\eta$, of Dibutoxymethane from 283.15 K to 403.15 K

T/K	η/mPa·s	$\Delta\eta$/mPa·s	T/K	η/mPa·s	$\Delta\eta$/mPa·s
283.15	1.236	−0.001	338.45	0.587	−0.002
285.35	1.192	0.000	343.05	0.558	−0.002
289.95	1.108	0.001	347.75	0.530	−0.001
293.65	1.047	0.001	353.65	0.498	−0.001
296.45	1.002	0.004	360.95	0.462	−0.000
301.35	0.940	−0.003	368.35	0.428	0.002
311.35	0.818	−0.002	373.95	0.409	−0.001
318.05	0.745	0.003	388.45	0.359	−0.000
323.15	0.700	0.001	397.65	0.330	0.002
332.75	0.624	0.001	403.15	0.320	−0.002
333.45	0.619	0.001			

Table 3. Experimental Results for Liquid Heat Capacity, C_p and ΔC_p, of Dibutoxymethane from 293.15 K to 416.15 K

T/K	C_p/J·mol^{-1}·K^{-1}	ΔC_p/J·mol^{-1}·K^{-1}	T/K	C_p/J·mol^{-1}·K^{-1}	ΔC_p/J·mol^{-1}·K^{-1}
293.15	329.84	−0.01	350.05	372.13	−0.01
299.15	334.31	0.05	366.65	384.42	−0.22
303.15	337.37	−0.01	368.45	385.50	0.00
309.15	341.87	−0.01	375.95	390.92	0.01
313.15	344.83	0.02	377.85	392.28	0.01
320.95	350.68	−0.01	385.25	397.61	−0.01
322.75	352.02	−0.02	387.15	398.95	0.01
331.85	358.72	0.03	404.15	411.02	0.04
339.05	364.09	−0.04	405.95	412.36	−0.02
340.95	365.44	0.01	415.15	418.84	−0.01
348.25	370.79	0.02	416.15	419.51	0.02

Table 4. Experimental Results for Liquid Thermal Conductivity, λ and $\Delta\lambda$, of Dibutoxymethane from 283.15 to 373.15 K

T/K	λ/mW/(m K)	$\Delta\lambda$/mW/(m K)	T/K	λ/mW/(m K)	$\Delta\lambda$/mW/(m K)
283.15	137.3	0.1	333.15	123.1	−0.1
293.15	134.4	0.0	343.15	120.4	0.0
303.15	131.5	−0.1	353.15	117.4	−0.2
313.15	128.7	−0.1	363.15	114.9	0.1
323.15	126.0	0.0	373.15	112.1	0.1

Table 5. Experimental Temperatures, *T*, Orthobaric Pressures, *P*, Precision Measures, *σ*T and *σ*P, Calculated Residuals, Δ*T* and Δ*P*, and Overall Measures of Data-Point Reproduction, *κ*, of Dibutoxymethane from 366.245 to 452.797 K

T / K	σ_T / K	ΔT / K	P / kPa	σ_P / kPa	ΔP / kPa	κ
366.245	0.021	−0.009	5.637	0.003	0.001	0.09
368.993	0.009	0.004	6.366	0.005	−0.001	−0.27
372.354	0.010	0.028	7.365	0.003	−0.002	1.12
374.145	0.010	0.016	7.936	0.004	−0.002	−0.73
377.220	0.013	−0.001	8.994	0.008	0.000	−0.03
377.516	0.010	0.008	9.108	0.003	−0.000	−0.27
381.499	0.012	0.003	10.686	0.006	0.000	−0.09
384.044	0.005	−0.013	11.785	0.003	0.001	1.32
386.220	0.005	−0.010	12.812	0.003	0.001	−1.92
389.313	0.005	0.021	14.459	0.004	−0.004	−1.85
390.768	0.009	−0.017	15.204	0.007	0.001	−0.91
394.234	0.010	0.037	17.317	0.002	−0.005	1.18
398.162	0.006	0.011	19.917	0.007	−0.002	−0.98
400.359	0.006	0.000	21.470	0.009	0.000	−0.13
403.058	0.008	−0.021	23.507	0.009	0.002	−1.26
408.800	0.010	0.000	28.532	0.008	−0.000	−0.02
409.858	0.010	−0.024	29.492	0.009	0.000	0.89
415.246	0.007	0.013	35.113	0.009	−0.005	0.94
419.503	0.010	0.017	40.047	0.009	−0.000	0.61
423.800	0.009	0.022	45.596	0.011	−0.002	0.96
427.447	0.009	−0.020	50.647	0.009	0.002	0.75
432.709	0.007	−0.003	58.894	0.011	0.000	−0.21
452.797	0.005	−0.001	100.225	0.008	0.000	−0.08

to oscillate around zero with satisfactory frequency. The calculated deviations (Table 5) in observed temperature (ΔT) and pressure (ΔP) show a consistently statistical pattern, and especially as regards temperature, they do not rise in the vicinity of the normal boiling point. This fact proves that the substance is thermally stable and shows no signs of decomposition as the temperature is increased. Indirectly, this fact is also a confirmation of the high purity of the sample used for the measurements. When expressed in common logarithms, the constants in the equation (A' = 5.75114, B' = 1298.562) are close to the average constants obtained for about 50 hydrocarbons.[11,12] The Antoine equation has been found to give reliable extrapolations to 200 kPa. The present equation is believed to permit predictions to within ±1 kPa or better at about 150 kPa. The correlation equations given for the remaining property data are valid within the experimental range.

Literature Cited

(1) French Pat., Fr. Demande FR 2,544,738, 1984 (CAS 102, 134803).

(2) Pedley, J. B.; Rylance, J.; Sussex, N. P. L. *Computer Analyzed Thermochemical Data. Organic and Organometallic Compounds*; University of Sussex: 1977.

(3) Ghysels, M. The Formals of the Primary Alcohols. *Bull. Soc. Chim. Belg.* **1924,** *33,* 57−78

(4) Kazaryan, L. Z.; Zaprosyan, T. O. Synthesis of Acetals of Aliphatic Aldehydes. *Izv. Akad. Nauk Arm. SSR, Khim. Nauki* **1961**, *14*, 585−589.

(5) Mamedov, G. Ch. Acetals of Formaldehyde. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Technol.* **1960**, *3*, 1053−1055.

(6) Normant, H.; Crisan, C. α-Halo Ethers I. Reaction of Metals. *Bull. Soc. Chim. Fr.* **1959**, 199−200.

(7) Vogel, A. J. Physical Properties and Chemical Constitution. Part XII. Ethers and Acetals. *J. Chem. Soc.* **1948**, 616−624.

(8) Palczewska-Tulińska, M.; Choliński, J.; Szafrański, A. M.; Wyrzykowska-Stankiewicz, D. Maximum-Likelihood Evaluation of Antoine Equation Constants for Vapor Pressures of Morpholine, *n*-Heptane, Cyclohexane and Methylcyclohexane. *Fluid Phase Equilib.* **1983**, *11*, 233−243.

(9) Palczewska-Tulińska, M.; Choliński, J.; Szafrański, A. M.; Wyrzykowska-Stankiewicz, D. Experimental Vapor Pressures and Maximum-Likelihood Antoine-Equation Constants for 1,1,1-Methoxydimethylpropane, Thiacyclopentane and 1,4-Butanediol. *Fluid Phase Equilib.* **1984**, *15*, 295−307.

(10) Choliński, J.; Palczewska-Tulińska, M.; Szafrański, A. M.; Wyrzykowska-Stankiewicz, D. A New Method of Parameter Adjustment and Diagnostic Checks on Gamma Models Used in VLE Calculations. *Chem. Eng. Sci.* **1981**, *36*, 173−181.

(11) Willingham, Ch. B.; Taylor, W. J.; Pignocco, J. M.; Rossini, F. D. Vapor Pressures and Boiling Points of Some Paraffin, Alkylcyclopentane, Alkylcyclohexane and Alkylbenzene Hydrocarbons. *J. Res. Natl. Bur. Stand.* **1945**, *35*, 219−243.

(12) Wyrzykowska-Stankiewicz, D.; Szafrański, A. M.; Rapacka, K. Evaluation of Antoine Equation Constants. *Proceedings of the IUPAC 3rd International Conference on Chemical Thermodynamics*, Baden, Austria; 1973; Vol. 2, pp 16−24.

Received for review February 23, 2000. Accepted May 1, 2000.

JE000070L