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# Vapour pressure and enthalpy of vaporization of aliphatic dialkyl carbonates

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## Abstract

Molar enthalpies of vaporization of aliphatic alkyl carbonates: dimethyl carbonate [616-38-6], diethyl carbonate [105-58-8], di-*n*-propyl carbonate [623-96-1], di-*n*-butyl carbonate [542-52-9], and dibenzyl carbonate [3459-92-5] were obtained from the temperature dependence of the vapour pressure measured by the transpiration method. A large number of the primary experimental results on temperature dependences of vapour pressures have been collected from the literature and have been treated uniformly in order to derive vaporization enthalpies of dialkyl carbonates at the reference temperature 298.15 K. An internal consistency check was performed on enthalpy of vaporization values for dialkyl carbonates studied in this work.

*Keywords:* Vapour pressure; Enthalpy of vaporization; Transpiration method; Carbonates

## 1. Introduction

Dialkyl carbonates are known as outstanding dipolar aprotic solvents widely utilized in electrochemical applications and extraction processes. Their excellent solvency, high flash and boiling temperatures, low toxicity, and evaporation rates make them attractive choices in many solvent applications. Dialkyl carbonates are biodegradable, non-corrosive, and relatively odourless materials, as well as being readily available from several solvent manufacturers. They are "safe" and environmentally friendly solvent alternatives to traditional products such as methylene chloride, aromatic solvents, and other high volatile and hazardous industrial solvents. In our recent work, we have identified advantages of propylene carbonate in asymmetric hydrogenation [1], and also for palladium-catalyzed substitution reactions [2].

Alkyl carbonates are high boiling liquids. Precise measurement of the vapour pressure of low-volatile compounds at ambient temperature is usually difficult, that is why the most of published data are referred to elevated temperatures close to the boiling point [3]. The transpiration method [4] used in this work provided a capability for the measurement of new vapour pressure data for dialkyl carbonates near ambient temperatures, where the data are especially relevant for the assessment of their fate and behaviour in the environment.

## 2. Experimental section

### 2.1. Materials

The liquid samples of dialkyl carbonates of 0.99 mass-fraction purity were obtained from Aldrich and Fluka and further purified by repetitive distillation in vacuum.

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Gas chromatography (GC) showed no traceable amounts of impurities in dialkyl carbonate samples after they were purified. The products were analyzed with a Hewlett-Packard gas chromatograph 5890 Series II with a flame ionization detector and Hewlett-Packard 3390A integrator. The dimensions of the capillary column HP-5 (stationary phase cross linked 5% PH ME silicone) were the following: the column length, inside diameter, and film thickness were 25 m, 0.32 mm, and 0.25 μm, respectively. The flow rate of a carrier gas (nitrogen) was $12.1\ \mathrm{cm^3 \cdot s^{-1}}$. The starting point for the GC temperature programme was $T = 323$ K with a heating rate of $0.167\ \mathrm{K \cdot s^{-1}}$ up until reaching 523 K temperature.

### 2.2. Vapour pressure measurements of alkyl carbonates

Vapour pressures of dialkyl carbonates were determined using the method of transpiration [4] in a saturated nitrogen stream. About 0.5 g of the sample was mixed with glass beads and placed in a thermostatted U-shaped tube having a length of 20 cm and a diameter of 0.5 cm. Glass beads with a diameter of the glass spheres of 1 mm provide a surface area large enough for rapid (vapour + liquid) equilibration. At constant temperature (±0.1 K), a nitrogen stream was passed through the U-tube and the transported amount of gaseous material was collected in a cooling trap. The flow rate of the nitrogen stream was measured using a soap bubble flow meter and was optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The amount of condensed substance was determined by GC analysis using an external standard (hydrocarbon $n$-$C_nH_{2n+2}$). The saturation vapour pressure $p_i^{\mathrm{sat}}$ at each temperature $T_i$ was calculated from the amount of the product collected within a definite period of time. Assuming that Dalton‘s law of partial pressures applied to the nitrogen stream saturated with the substance $i$ of interest is valid, values of $p_i^{\mathrm{sat}}$ were calculated with equation:

$$p_i^{\mathrm{sat}} = m_i \cdot R \cdot T_{\mathrm{a}} / V \cdot M_i; \quad V = V_{\mathrm{N_2}} + V_i; \quad (V_{\mathrm{N_2}} \text{»} V_i), \qquad (1)$$

where $R = 8.314472\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$; $m_i$ is the mass of the transported compound, $M_i$ is the molar mass of the compound, and $V_i$; its volume contribution to the gaseous phase. The $V_{\mathrm{N_2}}$ is the volume of the carrier gas and $T_{\mathrm{a}}$ is the temperature of the soap bubble meter. The volume of the carrier gas $V_{\mathrm{N_2}}$ was determined from the flow rate and the time measurement.

## 3. Results and discussion

### 3.1. Vapour pressure and vaporization enthalpies

Vapour pressures of alkyl carbonates measured in this work and enthalpies of vaporization (table 1) were treated with equations (2) and (3), respectively

TABLE 1
Experimental vapour pressures and enthalpy of vaporization of dialkyl carbonates measured by the transpiration method

| $T^a$/K | $m^b$/ mg | $V_{\mathrm{N_2}}{}^c$/ $\mathrm{dm^3}$ | $N_2$ flow/ $(\mathrm{dm^3 \cdot h^{-1}})$ | $p^d$/Pa | $(p_{\mathrm{exp}} - p_{\mathrm{calc}})$/ Pa | $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$/ $(\mathrm{kJ \cdot mol^{-1}})$ |
|---|---|---|---|---|---|---|
| *Dimethyl carbonate*; $\Delta_l^g H_m\ (298.15K) = (38.02 \pm 0.19)/(kJ \cdot mol^{-1})$ <br> $ln(p/Pa) = \frac{255.1}{R} - \frac{53945.8}{(R \cdot T/K)} - \frac{53.4}{R} ln\left(\frac{T/K}{298.15}\right)$ | | | | | | |
| 274.2 | 34.62 | 0.514 | 2.06 | 1918.4 | 6.6 | 39.31 |
| 275.0 | 35.81 | 0.514 | 2.06 | 1981.3 | −35.1 | 39.26 |
| 276.0 | 38.87 | 0.514 | 2.06 | 2143.5 | 4.4 | 39.21 |
| 276.9 | 41.42 | 0.514 | 2.06 | 2277.1 | 15.8 | 39.16 |
| 277.9 | 44.50 | 0.514 | 2.06 | 2433.8 | 29.9 | 39.11 |
| 280.7 | 52.48 | 0.514 | 2.06 | 2844.4 | −9.3 | 38.96 |
| 283.2 | 28.74 | 0.244 | 0.98 | 3273.5 | −32.5 | 38.82 |
| 285.8 | 33.93 | 0.244 | 0.98 | 3846.4 | 17.4 | 38.69 |
| 288.2 | 39.14 | 0.244 | 0.98 | 4424.4 | 40.1 | 38.56 |
| 290.8 | 43.67 | 0.242 | 0.97 | 4978.5 | −83.1 | 38.42 |
| 293.1 | 50.14 | 0.242 | 0.97 | 5709.8 | −23.1 | 38.30 |
| 295.7 | 59.28 | 0.242 | 0.97 | 6716.6 | 118.3 | 38.16 |
| 298.3 | 66.91 | 0.242 | 0.97 | 7570.4 | 18.3 | 38.02 |
| 300.7 | 75.64 | 0.242 | 0.97 | 8550.7 | 17.5 | 37.89 |
| 303.2 | 84.79 | 0.242 | 0.97 | 9675.8 | 9.0 | 37.75 |
| 304.1 | 87.56 | 0.242 | 0.97 | 9982.9 | −97.0 | 37.71 |
| *Diethyl carbonate*; $\Delta_l^g H_m\ (298.15K) = (44.35 \pm 0.22)/(kJ \cdot mol^{-1})$ <br> $ln(p/Pa) = \frac{276.3}{R} - \frac{64238.2}{(R \cdot T/K)} - \frac{66.7}{R} ln\left(\frac{T/K}{298.15}\right)$ | | | | | | |
| 273.1 | 7.953 | 0.592 | 2.37 | 287.6 | 6.7 | 46.03 |
| 273.3 | 18.514 | 1.374 | 5.50 | 288.3 | 3.2 | 46.01 |
| 274.0 | 8.420 | 0.592 | 2.37 | 304.3 | 2.9 | 45.96 |
| 274.0 | 19.863 | 1.374 | 5.50 | 307.7 | 7.5 | 45.97 |
| 275.0 | 21.299 | 1.374 | 5.50 | 328.9 | 5.8 | 45.90 |
| 276.2 | 22.864 | 1.374 | 5.50 | 352.5 | 0.0 | 45.82 |
| 276.5 | 10.240 | 0.604 | 2.37 | 361.9 | 1.7 | 45.80 |
| 277.1 | 24.512 | 1.374 | 5.50 | 377.1 | 1.0 | 45.76 |
| 278.1 | 11.499 | 0.592 | 2.37 | 412.2 | 8.3 | 45.69 |
| 278.2 | 13.506 | 0.706 | 2.81 | 406.5 | −0.3 | 45.69 |
| 282.4 | 17.560 | 0.660 | 2.64 | 558.3 | 13.0 | 45.41 |
| 283.1 | 16.215 | 0.592 | 2.37 | 579.3 | 5.4 | 45.36 |
| 283.3 | 18.922 | 0.706 | 2.81 | 558.7 | −21.1 | 45.35 |
| 285.0 | 17.716 | 0.592 | 2.37 | 632.1 | −20.4 | 45.23 |
| 286.8 | 24.696 | 0.664 | 2.66 | 776.9 | 41.5 | 45.11 |
| 288.2 | 24.013 | 0.629 | 2.22 | 790.7 | −12.7 | 45.02 |
| 288.3 | 23.394 | 0.592 | 2.37 | 825.8 | 15.5 | 45.01 |
| 288.4 | 26.338 | 0.702 | 2.81 | 784.1 | −29.9 | 45.01 |
| 291.8 | 32.551 | 0.669 | 2.66 | 1016.6 | 4.1 | 44.78 |
| 293.0 | 28.610 | 0.557 | 2.22 | 1051.2 | −40.8 | 44.70 |
| 293.1 | 31.329 | 0.628 | 2.49 | 1041.6 | −57.2 | 44.69 |
| 293.1 | 27.954 | 0.555 | 2.22 | 1033.0 | −65.8 | 44.69 |
| 293.1 | 27.954 | 0.555 | 2.22 | 1037.9 | −60.9 | 44.69 |
| 293.2 | 37.542 | 0.725 | 2.81 | 1078.0 | −27.7 | 44.69 |
| 293.3 | 12.194 | 0.241 | 0.96 | 1064.2 | −52.0 | 44.68 |
| 296.8 | 46.132 | 0.664 | 2.66 | 1447.4 | 67.1 | 44.44 |
| 298.0 | 44.372 | 0.624 | 2.49 | 1485.1 | 1.0 | 44.36 |
| 298.1 | 45.614 | 0.633 | 2.53 | 1516.3 | 23.3 | 44.36 |
| 298.1 | 17.453 | 0.251 | 1.00 | 1454.8 | −42.7 | 44.35 |
| 298.2 | 18.168 | 0.249 | 0.96 | 1535.6 | 33.5 | 44.35 |
| 301.8 | 22.700 | 0.248 | 0.99 | 1907.1 | 48.8 | 44.11 |
| 303.0 | 24.276 | 0.251 | 1.00 | 2010.2 | 18.0 | 44.03 |
| 303.1 | 27.341 | 0.284 | 1.02 | 2021.1 | 17.3 | 44.02 |
| 303.1 | 24.670 | 0.251 | 1.01 | 2056.5 | 52.7 | 44.02 |
| 303.3 | 22.812 | 0.241 | 0.96 | 1988.0 | −39.0 | 44.01 |
| 306.8 | 29.196 | 0.248 | 0.99 | 2453.2 | −19.2 | 43.78 |
| 307.8 | 32.479 | 0.251 | 1.00 | 2688.5 | 67.1 | 43.71 |
| 308.2 | 30.486 | 0.242 | 0.96 | 2635.6 | −37.1 | 43.68 |
| 308.2 | 32.644 | 0.256 | 1.02 | 2688.9 | 16.2 | 43.68 |

(*continued on next page*)