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# Vapor Pressures of Hexanal, 2-Methylcyclohexanone, and 2-Cyclohexen-1-one

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The saturated vapor pressures were measured for samples of mole fraction purity of 99.98 % hexanal, 2-methylcyclohexane, and 2-cyclohexen-1-one over wide temperature ranges by comparative ebulliometry. Measurements were made over the temperature range of (322.27 to 402.17) K for hexanal, (338.76 to 436.94) K for 2-methylcyclohexanone, and (350.40 to 445.00) K for 2-cyclohexen-1-one, respectively. The experimental data were correlated, and overall measures of data reproducibility are given. The results are compared with literature data.

## Introduction

Reliable physical property data are required for efficient design in chemical engineering. Three oxygen compounds (hexanal, 2-methylcyclohexanone, and 2-cyclohexen-1-one) being of industrial interest were considered. These compounds, for example, are involved in the caprolactam production process. The reliable simulation of all the unit, among other data, requires reliable saturated vapor pressures of all compounds in relatively wide temperature range.

In this work, the saturated vapor pressures of hexanal over the temperature range from (322.27 to 402.17) K, of 2-methylcyclohexanone over the temperature range from (338.76 to 436.94) K, and of 2-cyclohexen-1-one over the temperature range from (350.40 to 445.00) K were measured and correlated with the Antoine equation.

## Experimental Section

***Chemicals.*** Samples (of hexanal, 2-methylcyclohexane, and 2-cyclohexen-1-one) of certified mole fraction purity of 99.98 % were used as supplied by CHEMIPAN R & D Laboratories (Warsaw, Poland).

***Apparatus and Procedure*****.** Saturated vapor pressure was measured over a temperature range of (322.27 to 402.17) K for hexanal, (338.76 to 436.94) K for 2-methylcyclohexanone, and (350.40 to 445.00) K for 2-cyclohexen-1-one, respectively. The comparative ebulliometric technique comprising a dynamic twin-ebulliometer assembly was used as described elsewhere.[1] Hexanal can be easily oxidated by oxygen from air, so special precautions have been adopted to prevent contact between air and measured sample. To this end, all operations were performed in dry nitrogen atmosphere. Temperature was measured on ITS-90 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:

for hexanal

$$\ln(P/\mathrm{kPa}) = 14.42607 - \frac{3390.60}{T/\mathrm{K} - 57.024} \tag{1}$$

for 2-methylcyclohexanone

$$\ln(P/\mathrm{kPa}) = 14.06663 - \frac{3517.58}{T/\mathrm{K} - 65.272} \tag{2}$$

for 2-cyclohexen-1-one

$$\ln(P/\mathrm{kPa}) = 14.12592 - \frac{3587.84}{T/\mathrm{K} - 67.987} \tag{3}$$

the maximum likelihood method was used as described in more detail elsewhere.[1,2] Tables 1(for hexanal), 2 (for 2-methylcyclohexanone), and 3 (for 2-cyclohexen-1-one) list the observed ($T_i$, $P_i$) data pairs, their estimated precision measures ($\sigma_{T_i}$, $\sigma_{P_i}$) and the deviations ($\Delta T_i$, $\Delta P_i$) between the observed and calculated variables. The $\Delta T_i$ and $\Delta P_i$ 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 $\Delta T_i$ nor $\Delta P_i$ alone is adequately representative as an overall measure of reproduction for an individual data point, we suggested[1]

$$\kappa^{s}_{i} = \mathrm{sgn}(\Delta T_i)\kappa_i/\hat{\sigma} \tag{4}$$

where, for the present case

$$\kappa_i = [(\Delta P_i/\sigma_{P_i})^2 + (\Delta T_i/\sigma_{T_i})^2]^{1/2} \tag{5}$$

as an overall measure of data-point reproduction, where $\kappa_i$ is the distance between the $i$th observed and estimated data points in the ($P$, $T$) space, $\sigma_T$ and $\sigma_P$, are adopted as length units. The $\kappa_i^s$ values are seen (eq 4) to be scaled with respect to $\hat{\sigma}$ (i.e., to the standard deviation of $\kappa_i$ given by)

$$\hat{\sigma} = \left[\sum_{i=1}^{n} \kappa_i^{\,2}/(n-3)\right]^{1/2} \tag{6}$$

where $n$ is the number of experimental points. The sign of $\Delta T_i$

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**Table 1. Experimental Temperatures $T$, Orthobaric Pressures $P$, Precision Measures $\sigma_T$ and $\sigma_P$, Calculated Residuals $\Delta T$ (= $T_{exp} - T_{calc}$) and $\Delta P$ (= $P_{exp} - P_{calc}$), and Overall Measures of Data-Point Reproduction, $\kappa$, of Hexanal**

| $T$/K | $\sigma_T$/K | $\Delta T$/K | $P$/kPa | $\sigma_P$/kPa | $\Delta P$/kPa | $\kappa$ |
|---|---|---|---|---|---|---|
| 322.27 | 0.01 | −0.01 | 5.184 | 0.007 | 0.011 | −0.61 |
| 325.43 | 0.01 | 0.01 | 6.001 | 0.007 | −0.009 | 0.54 |
| 327.84 | 0.02 | 0.03 | 6.711 | 0.006 | −0.008 | 0.70 |
| 330.22 | 0.01 | 0.00 | 7.510 | 0.007 | 0.006 | −0.37 |
| 333.56 | 0.02 | 0.00 | 8.713 | 0.006 | −0.001 | 0.10 |
| 338.89 | 0.01 | 0.00 | 10.990 | 0.002 | 0.000 | −0.02 |
| 342.12 | 0.01 | 0.01 | 12.590 | 0.003 | −0.001 | 0.27 |
| 347.22 | 0.01 | −0.05 | 15.555 | 0.001 | 0.001 | −1.95 |
| 353.44 | 0.01 | 0.05 | 19.795 | 0.002 | −0.003 | 1.87 |
| 360.11 | 0.02 | 0.07 | 25.445 | 0.001 | 0.000 | 1.33 |
| 366.28 | 0.01 | −0.01 | 31.908 | 0.005 | 0.003 | −0.49 |
| 371.95 | 0.01 | −0.01 | 38.875 | 0.007 | 0.005 | −0.59 |
| 377.98 | 0.01 | 0.00 | 47.562 | 0.007 | 0.000 | −0.02 |
| 402.17 | 0.01 | 0.00 | 99.716 | 0.011 | −0.001 | 0.10 |

**Table 2. Experimental Temperatures $T$, Orthobaric Pressures $P$, Precision Measures $\sigma_T$ and $\sigma_P$, Calculated Residuals $\Delta T$ (= $T_{exp} - T_{calc}$) and $\Delta P$ (= $P_{exp} - P_{calc}$), and Overall Measures of Data-Point Reproduction, $\kappa$, of 2-Methylcyclohexanone**

| $T$/K | $\sigma_T$/K | $\Delta T$/K | $P$/kPa | $\sigma_P$/kPa | $\Delta P$/kPa | $\kappa$ |
|---|---|---|---|---|---|---|
| 338.76 | 0.06 | 0.01 | 3.333 | 0.007 | −0.001 | 0.20 |
| 342.20 | 0.06 | 0.01 | 3.912 | 0.006 | 0.000 | 0.12 |
| 348.85 | 0.06 | 0.02 | 5.267 | 0.008 | −0.001 | 0.24 |
| 350.96 | 0.03 | 0.06 | 5.763 | 0.001 | 0.000 | 1.55 |
| 353.34 | 0.01 | −0.02 | 6.401 | 0.001 | 0.001 | −1.33 |
| 355.93 | 0.01 | 0.00 | 7.129 | 0.003 | −0.001 | 0.47 |
| 358.53 | 0.01 | −0.01 | 7.941 | 0.001 | 0.000 | −0.42 |
| 360.73 | 0.01 | 0.01 | 8.678 | 0.001 | 0.000 | 0.65 |
| 363.09 | 0.01 | −0.01 | 9.543 | 0.003 | 0.001 | −0.54 |
| 366.66 | 0.02 | −0.01 | 10.980 | 0.004 | 0.001 | −0.66 |
| 369.65 | 0.01 | 0.00 | 12.305 | 0.002 | 0.000 | 0.04 |
| 372.70 | 0.01 | 0.02 | 13.788 | 0.002 | −0.002 | 1.77 |
| 376.36 | 0.01 | 0.00 | 15.794 | 0.006 | 0.003 | −0.51 |
| 381.72 | 0.01 | 0.00 | 19.121 | 0.001 | 0.000 | 0.07 |
| 384.91 | 0.01 | 0.00 | 21.366 | 0.001 | 0.000 | −0.11 |
| 389.42 | 0.01 | 0.00 | 24.903 | 0.001 | 0.000 | −0.28 |
| 394.59 | 0.01 | −0.01 | 29.530 | 0.002 | 0.000 | −0.42 |
| 398.32 | 0.01 | −0.01 | 33.288 | 0.007 | 0.003 | −0.71 |
| 399.98 | 0.01 | 0.01 | 35.050 | 0.010 | −0.007 | 0.88 |
| 408.17 | 0.01 | 0.03 | 45.028 | 0.005 | −0.005 | 2.44 |
| 411.64 | 0.01 | −0.02 | 49.985 | 0.006 | 0.005 | −1.77 |
| 414.00 | 0.01 | −0.01 | 53.525 | 0.006 | 0.003 | −1.02 |
| 418.28 | 0.01 | 0.00 | 60.460 | 0.008 | −0.001 | 0.18 |
| 436.94 | 0.01 | 0.00 | 99.707 | 0.005 | 0.000 | 0.30 |

has been attributed to $\kappa_i$ to have the experimental point located ”below” or ”above” the response curve. When systematical errors are absent, sign of $\kappa_i^s$ should be randomly distributed and absolute values should be about unity; large $\kappa_i$ values ($\gg$1) may indicate outliers. Easy measure of the randomness of $\kappa_i^s$ is number of sign changes test. If two neighboring $\kappa_i^s$ have opposite signs, then one speaks of a sign change. Total number of sign changes should be roughly equal to $n/2 \pm (n/2)^{1/2}$ (limits at 68 % probability level). The corresponding values are 9 (5 to 9) for hexanal, 12 (9 to 15) for 2-methylcyclohexanone, and 9 (6 to 12) for 2-cyclohexen-1-one, where values in parentheses are limits calculated at 68 % probability level.

The calculated deviations (Tables 1 to 3) in observed temperature ($\Delta T$) and pressure ($\Delta P$) show a consistently statistical pattern and, especially as regards temperature, they do not rise in the vicinity to the normal boiling point. This shows 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.

**Table 3. Experimental Temperatures $T$, Orthobaric Pressures $P$, Precision Measures $\sigma_T$ and $\sigma_P$, Calculated Residuals $\Delta T$ (= $T_{exp} - T_{calc}$) and $\Delta P$ (= $P_{exp} - P_{calc}$), and Overall Measures of Data-Point Reproduction, $\kappa$, of 2-Cyclohexen-1-one**

| $T$/K | $\sigma_T$/K | $\Delta T$/K | $P$/kPa | $\sigma_P$/kPa | $\Delta P$/kPa | $\kappa$ |
|---|---|---|---|---|---|---|
| 350.40 | 0.01 | −0.01 | 4.147 | 0.001 | 0.001 | −0.46 |
| 353.66 | 0.01 | 0.01 | 4.786 | 0.002 | −0.002 | 0.57 |
| 357.56 | 0.03 | 0.05 | 5.662 | 0.001 | 0.000 | 0.55 |
| 361.48 | 0.02 | −0.04 | 6.709 | 0.003 | 0.003 | −0.79 |
| 366.16 | 0.03 | 0.05 | 8.095 | 0.002 | −0.001 | 0.55 |
| 370.32 | 0.01 | −0.02 | 9.581 | 0.002 | 0.002 | −0.81 |
| 374.97 | 0.01 | −0.01 | 11.462 | 0.002 | 0.001 | −0.44 |
| 379.00 | 0.01 | 0.01 | 13.312 | 0.011 | −0.014 | 0.50 |
| 380.50 | 0.01 | 0.01 | 14.060 | 0.010 | −0.022 | 0.87 |
| 386.63 | 0.02 | 0.06 | 17.526 | 0.006 | −0.008 | 1.11 |
| 388.40 | 0.01 | 0.02 | 18.676 | 0.005 | −0.008 | 0.91 |
| 391.77 | 0.01 | 0.03 | 20.949 | 0.010 | −0.039 | 1.69 |
| 397.16 | 0.01 | −0.02 | 25.204 | 0.004 | 0.003 | −0.60 |
| 404.53 | 0.01 | −0.03 | 32.026 | 0.007 | 0.015 | −1.34 |
| 407.95 | 0.01 | 0.03 | 35.563 | 0.005 | −0.006 | 1.03 |
| 410.86 | 0.01 | −0.04 | 39.010 | 0.009 | 0.028 | −1.76 |
| 424.23 | 0.02 | 0.01 | 57.636 | 0.012 | −0.003 | 0.26 |
| 445.00 | 0.01 | 0.01 | 100.399 | 0.018 | −0.010 | 0.33 |

## Results and Discussion

Saturated vapor pressures for hexanal, 2-methylcyclohexanone, and 2-cyclohexen-1-one can be compared with corresponding literature data. Deviations between the experimental data, both the newly measured and taken from literature, and the values calculated with relevant equations with parameters fitted to the new data versus temperature are presented in Figures 1 to 3.

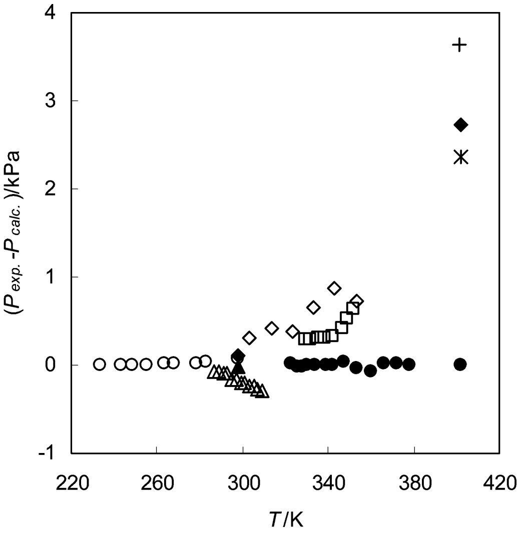

**Figure 1.** Hexanal deviations between the experimental saturated vapor pressures and the values calculated with eq 1 vs temperature: ●, this work; *, Rossini et al.;[3] +, Ogorodnikov et al.;[14] ◆, D’yakova et al.;[4] ◇, Hahn;[5] ▲, Caccioni et al.;[6] □, Wichterle;[7] △, Verevkin et al.;[8] ○, Covarrubias-Cervantes et al.[9]

For hexanal, Rossini et al.[3] reported value of the normal boiling point, D’yakova et al.[4] reported saturated vapor pressures at (298.15 and 401.77) K, Hahn and Moerke[5] reported saturated vapor pressures in the range (303.3 to 353.5) K, Caccioni et al.[6] reported value of the boiling point at 298.15 K, Wichterle[7] reported saturated vapor pressures at (329.0 to 351.5) K, Verevkin et al.[8] reported saturated vapor pressures at (286.8 to 309.2) K, Covarrubias-Cervantes et al.[9] reported saturated vapor pressures at (233.15 to 298.15) K. There exist excellent agreement of our data with these of Covarrubias-Cervantes et al., Caccioni et al., and lower value reported by D’yakova et

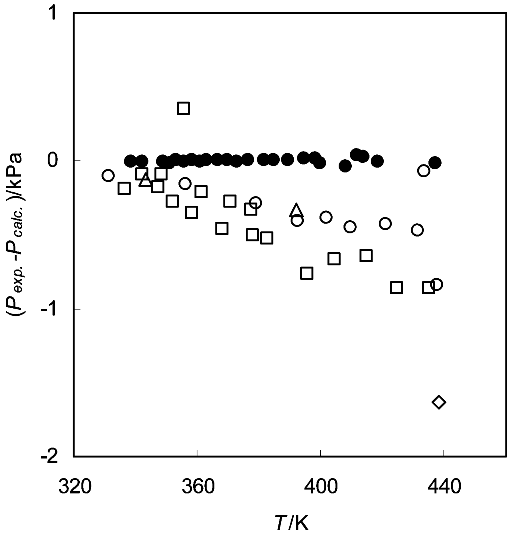

**Figure 2.** 2-Methylcyclohexanone deviations between the experimental saturated vapor pressures and the values calculated with eq 2 vs temperature: ●, this work; □, Stoeck and Roscher;[10] ○, Burguet et al.[11] (saturated vapor pressure measurements); △, Burguet et al.[11] (VLE measurements).

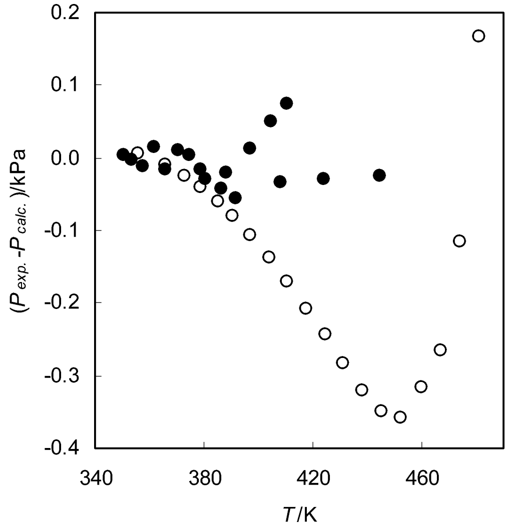

**Figure 3.** 2-Cyclohexen-1-one deviations between the experimental saturated vapor pressures and the values calculated with eq 3 vs temperature: ●, this work; ○, Steele et al.[15]

al. Data of Verevkin et al. and Wichterle exhibit small systematic deviations from our data. These two data sets have deviations calculated using our Antoine parameters as a reference in opposite directions when compared to each other.

For 2-methylcyclohexanone Stoeck and Roscher[10] reported saturated vapor pressures at (336.46 and 435.36) K, Burguet et al.[11] reported saturated vapor pressures at (331.35 and 438.20) K, and two distinct boiling points can be adopted from VLE measurements at (4.00 and 26.66) kPa, Ogorodnikov et al.[14] and reference[12] reported value of the normal boiling point. At lower temperature data of Stoeck and Roscher, the Burguet et al. data coincide with our measurements. Systematically increasing discrepancies are observed with the increase of temperature. As can be seen from Figure 2, smaller deviations are observed for newer data.

For 2-cyclohexen-1-one, Steele et al.[15] reported saturated vapor pressures at (334.844 to 481.361) K. In the temperature range (to 390) K our data agreed with these of Steele et al. within experimental error and then more significant, systematic deviation is observed down to −0.358 kPa (0.29 %) at temperature of 452.59 K. At higher temperatures, deviations between our extrapolated values and experimental data of Steele et al. rapidly diminish. In references 13 and 16, values of the normal boiling point are reported. Both these values significantly deviate from both our and Steele et al. estimates for the normal boiling point; therefore, both points have been ignored when preparing the residual graph given in Figure 3.

## Literature Cited

(1) 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.
(2) 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.
(3) Rossini, F. D.; Pitzer, K. S.; Arnett, R. L.; Braun, R. M.; Pimentel, G. C. *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*; Carnegie Press: Pittsburgh, 1953.
(4) D'yakova, G. N.; Korichev, G. L.; Korkhov, A. D.; Vasil'eva, T. F.; Vasil'ev, I. A. Vapor pressure investigation of aliphatic aldehydes. *Zh. Prikl. Khim.* (*J. Appl. Chem. USSR*) **1981**, *54*, 1644−1646.
(5) Hahn, J.; Moerke, K. Leuna Protocol, 1984, p 10161.
(6) Caccioni, D. R. L.; Gardani, F.; Lanciotti, R.; Guerzoni, M. E. Antifungal activity of natural volatile compounds in relation to their vapour pressure. *Sci. Aliments* **1997**, *17*, 21−34.
(7) Wichterle, I. Private communication, 2000.
(8) Verevkin, S. P.; Krasnykh, E. L.; Vasiltsova, T. V.; Koutek, B.; Doubsky, J.; Heintz, A. Vapor pressures and enthalpies of vaporization of a series of the linear aliphatic aldehydes. *Fluid Phase Equilib.* **2003**, *206*, 331−339.
(9) Covarrubias-Cervantes, M.; Mokbel, I.; Champion, D.; Jose, J.; Voilley, A. Saturated vapour pressure of aroma compounds at various temperatures. *Food Chem.* **2004**, *85*, 221−229.
(10) Stoeck, S.; Roscher, T. Leuna Protocol, 1981; p 4281.
(11) Burguet, M. C.; Montón, J. B.; Sanchotello, M.; Vázquez, M. I. Vapor−liquid equilibria of cyclohexanone + cyclohexanol and cyclohexanone + 2-methylcyclohexanone systems at 4.00 and 26.66 kPa. *J. Chem. Eng. Data* **1993**, *38*, 328−331.
(12) *Physicochemical Handbook*; WNT−Scientific-Technical Publishers: Warsaw, 1962 (in Polish).
(13) Weast, R. C., Grasselli, J. G., Eds. *CRC Handbook of Data on Organic Compounds*, 2nd ed.; CRC Press: Boca Raton, FL, 1989.
(14) Ogorodnikov, S. K.; Lesteva, T. M.; Kogan, V. B. *Azeotropic Mixtures. Handbook*; Khimia: Leningrad, 1971 (in Russian).
(15) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A. Vapor pressure, heat capacity, and density along the saturation line, measurements for cyclohexanol, 2-cyclohexen-1-one, 1,2-dichloropropane, 1,4-di-*tert*-butylbenzene, (±)-2-ethylhexanoic acid, 2-(methylamino)-ethanol, perfluoro-*n*-heptane, and sulfolane. *J. Chem. Eng. Data* **1997**, *42*, 1021−1036.
(16) *Aldrich Catalogue Handbook of Fine Chemicals*; Sigma-Aldrich: Poland.

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