Convenient Method for the Estimation of Vapor Pressure of Some Organic Compounds

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Abstract

Relation between temperature and vapor pressure for organic compounds was investigated and the curve fitting for the data was carried out. The vapor pressure \((P/\text{mmHg})\) fitted well to the polynomials of the fifth degree in temperature \((t/\degree C)\). The values of vapor pressure estimated from the fitted equation coincide with those estimated from the Antoine's equation. The present fitting method is convenient to estimate the vapor pressure of organic compounds of which coefficients in the Antoine's equation are unknown.

1. Introduction

The authors studied the sorption of volatile organic compounds onto chemical and natural fibers and found that the fibers were identified by the GC analysis of the adsorbed compounds.\(^1\)\(^2\) Vapor pressure of organic compounds is considered to be one of the important factors for the discussion of the sorption property. But, vapor pressure of an organic compound at a definite temperature is not always obtained from literatures. Though the Antoine's equation is useful for this purpose, the coefficients in this equation are not given for all of the organic compound. On the other hand, we observed the fading of azo dyes in the reaction with sodium hypochlorite and estimated the equation between the absorbance of the reaction mixture and reaction time by the curve fitting. The initial reaction rate was estimated very easily from the fitted equation.\(^3\) In the present study, the relation between vapor pressure and temperature of organic compounds was investigated using the values in the references and those obtained experimentally to find a convenient method to estimate the vapor pressure.

2. Experimental

2.1 Reagents

Commercial guaranteed grade of \(N, N\)-dimethylformamide (DMF), decane, \(o\)-dichlorobenzene (\(o\)-DCB), ethanol (EtOH), dioxane, methyl salicylate and dichloro acetic acid (DCA) were refluxed over usual drying agents and fractionally distilled.
from the following Antoine’s equation,
\[ \log\left(\frac{P}{\text{mmHg}}\right) = A - \frac{B}{C + t(\degree C)} \] (1)
where \( A, B \) and \( C \) are constants inherent for each compound. But, we can see these constants for only 50% of organic compounds in the reference, Kagaku Binran.\(^4\) Therefore, we investigated the relation between vapor pressure and temperature for organic compounds in order to know another estimation method for the vapor pressure.

First, vapor pressures were plotted against temperatures for each of five compounds, EtOH, DMF, \( o \)-DCB, dioxane and decane as given in Figures 1-5, where plots are indicated with circles. The curve fitting was examined for these data and it was found that the vapor pressure \( (P/\text{mmHg}) \) was given by the following polynomial of the fifth degree in temperature \( (t/\degree C) \),
\[ P = a_0 + a_1t + a_2t^2 + a_3t^3 + a_4t^4 + a_5t^5 \] (2)

3. Results and Discussion

In general, vapor pressure of an organic compound at a given temperature can be estimated from the following Antoine’s equation,

\[ \log(P/\text{mmHg}) = A - \frac{B}{C + t(\degree C)} \] (1)

where \( A, B \) and \( C \) are constants inherent for each compound. But, we can see these constants for only 50% of organic compounds in the reference, Kagaku Binran.\(^4\) Therefore, we investigated the relation between vapor pressure and temperature for organic compounds in order to know another estimation method for the vapor pressure.

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Fig. 1 Plot between vapor pressure and temperature and the fitted curve with the data for ethanol.
Fig. 2 Plot between vapor pressure and temperature and the fitted curve with the data for DMF.

Fig. 3 Plot between vapor pressure and temperature and the fitted curve with the data for o-DCB.
Fig. 4 Plot between vapor pressure and temperature and the fitted curve with the data for dioxane.

Fig. 5 Plot between vapor pressure and temperature and the fitted curve with the data for decane.
Fig. 6 Plot between vapor pressure and temperature and the fitted curve with the data for methyl salicylate.

Fig. 7 Plot between vapor pressure and temperature and the fitted curve with the data for DCA.
Table 1 Coefficients in fitted equations

<table>
<thead>
<tr>
<th>Compound</th>
<th>( a_0 )</th>
<th>( a_1 )</th>
<th>( a_2 \times 10^2 )</th>
<th>( a_3 \times 10^4 )</th>
<th>( a_4 \times 10^6 )</th>
<th>( a_5 \times 10^8 )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtOH</td>
<td>12.02</td>
<td>0.6903</td>
<td>2.389</td>
<td>5.094</td>
<td>4.614</td>
<td>3.853</td>
<td>1.000</td>
</tr>
<tr>
<td>DMF</td>
<td>0.1342</td>
<td>0.8413</td>
<td>-6.456</td>
<td>19.658</td>
<td>-21.86</td>
<td>8.445</td>
<td>1.000</td>
</tr>
<tr>
<td>o-DCB</td>
<td>0.9793</td>
<td>-0.05810</td>
<td>0.3253</td>
<td>-0.2351</td>
<td>0.3990</td>
<td>0.1982</td>
<td>1.000</td>
</tr>
<tr>
<td>Dioxane</td>
<td>10.02</td>
<td>0.5430</td>
<td>1.879</td>
<td>2.616</td>
<td>-0.2129</td>
<td>2.368</td>
<td>1.000</td>
</tr>
<tr>
<td>Decane</td>
<td>0.02031</td>
<td>0.1489</td>
<td>-0.7667</td>
<td>1.796</td>
<td>-1.046</td>
<td>0.6126</td>
<td>1.000</td>
</tr>
<tr>
<td>Methyl Sal.</td>
<td>-0.004314</td>
<td>0.1015</td>
<td>-0.3815</td>
<td>0.5747</td>
<td>-0.3976</td>
<td>0.2302</td>
<td>1.000</td>
</tr>
<tr>
<td>DCA</td>
<td>-0.01276</td>
<td>0.5712</td>
<td>-2.620</td>
<td>4.363</td>
<td>-3.103</td>
<td>1.032</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Table 2 Vapor pressure estimated from the fitted equation (2) and the Antoine's equation (1)

<table>
<thead>
<tr>
<th>Compound</th>
<th>EtOH</th>
<th>DMF</th>
<th>o-DCB</th>
<th>Dioxane</th>
<th>Decane</th>
<th>Methyl Sal.</th>
<th>DCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P ) at 25°C calcd. from (2)</td>
<td>59.30</td>
<td>3.82</td>
<td>1.37</td>
<td>38.80</td>
<td>1.40</td>
<td>0.875</td>
<td>3.60</td>
</tr>
<tr>
<td>( P ) at 25°C calcd. from (1)</td>
<td>59.20</td>
<td>3.76</td>
<td>2.41</td>
<td>35.20</td>
<td>1.30</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( P/bp ) calcd. from (2)*</td>
<td>760/78.3</td>
<td>760/153</td>
<td>760/180.4</td>
<td>760/101.3</td>
<td>760/174.12</td>
<td>759/223.2</td>
<td>760/194.4</td>
</tr>
<tr>
<td>( P/bp ) calcd. from (1)</td>
<td>759/78.3</td>
<td>753/153</td>
<td>771/180.4</td>
<td>759/101.3</td>
<td>760/174.12</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

*\( P/bp \) means vapor pressure \( P \) at boiling point \( bp \).

where \( a_0, a_1, a_2, a_3, a_4 \) and \( a_5 \) are regression coefficients. The fitted equation is indicated by curves in Figs. 1-5. The coefficients and the square of correlation coefficient, \( R^2 \) (coefficient of determination) are given in Table 1. In each analysis, \( R^2 \) was 1.00. When no data were given in the temperature range where \( P \) seemed close to zero, the fitted equation intended to give minus value of \( P \). In order to avoid this discrepancy, \( P = 0 \) at 0 °C and presumed \( P \) values at low temperatures were used for the curve fitting. The authors examined the sorption of these five compounds onto polymer substances mainly at 25 °C. Table 2 gives the vapor pressure at 25 °C for each compound estimated from the fitted equation. Values of \( P \) at 25 °C estimated from the Antoine's equation were also given in Table 2. The constants in the Antoine's equation for the five compounds were obtained from the literature. We can see considerable agreement between the values calculated from the fitted equation (2) and those from the Antoine's equation (1). The most reliable value of \( P \) should be 760 mmHg at boiling point (bp) for each compound. The vapor pressure at bp for each compound was estimated from the equations (1) and (2). The fitted equation gave the vapor pressure, 760 mmHg for EtOH, DMF, o-DCB, dioxane and decane, while the Antoine's equation gave 753 mmHg and 771 mmHg for DMF and o-DCB, respectively. This fact suggests the present curve fitting is very useful. When the constants in the Antoine's equation are not obtained from the literature, the present method is very convenient for the estimation of \( P \) at a given temperature. For instance, the constants in the Antoine's equation for methyl salicylate and DCA are not given but several data of \( P \) are given in the literature. The values of \( P \) were plotted against temperatures and the curve fitting was made as shown in Figs. 6 and 7. The coefficients of the fitted equations are given in Table 1. These equations give the values of \( P \) at 25 °C and bp.
as given in Table 2.

4. Conclusion

Reference and experimental data of vapor pressure (P/mmHg) of some organic compounds were given by the polynomials of the fifth degree in temperature (t/°C). The fitted equation is very convenient for the estimation of vapor pressure of organic compounds of which constants in the Antoine’s equation are unknown.

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References