Original Article

Thermodynamic Estimation of Vapor Pressures for Carbamate Pesticides

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Vapor pressures of carbamate and thiocarbamate pesticides were estimated from their chemical structures by using the newly developed thermodynamic equations. The equations were derived from the modified Watson method by optimizing a parameter and introducing the concept of a number of possible hydrogen-bonding sites for better estimation of vapor pressures. This method could successfully estimate the vapor pressures of the tested pesticides and correctly predict vapor pressures, ranging from \(10^{-5}\) to \(10^1\) Pa at 298 K, of other pesticides not being utilized in the optimization procedure.

Key words: carbamates, estimation of vapor pressure, modified Watson method.

INTRODUCTION

Vapor pressure \(P_{vp}\) is one of the basic and important physicochemical parameters for predicting atmospheric concentration of a pesticide in computer simulation. Although the various measurement techniques have been developed, they are difficult and cumbersome to be applied to a pesticide possessing a low vapor pressure below 1 Pa. Therefore, the convenient methods of estimation have been proposed instead by some groups.\(^1,2\)

Two estimation methods based on the Clausius-Clapeyron equation evaluating \(P_{vp}\) values of organic compounds have been developed by Grain.\(^3\) One of them originates from the Antoine equation being generally applicable to chemicals in liquid and gas phases whose log \(P_{vp}\) values range from \(-0.88\) to 5.0. The other method is the modified Watson method where temperature dependency of enthalpy of vaporization \(\Delta H_v\) is incorporated in the Clausius-Clapeyron equation and is applicable to the log \(P_{vp}\) value of liquid and solid ranging from \(-4.88\) to 5.0. This method is recommended to estimate the \(P_{vp}\) value of a chemical in the OECD guideline\(^4\) and, for example, the \(P_{vp}\) values of benzene and DDT estimated by this method were in good agreement with the experimental values.\(^5\) Incidentally, the \(P_{vp}\) values of benzene and liquid chlorinated derivatives measured by the generator column method were satisfactorily predicted by the modified Watson method with the deviations of \(\pm 20\%\), but not for solid compounds.\(^5\) The observed error for solid might stem from an inappropriate exponent \(m\) in estimating \(\Delta H_v\) and was reduced by a factor of less than four when the \(m\) values was adjusted in his study. Burkhard has utilized the modified Watson method in computing \(P_{vp}\) values of 15 polychlorinated biphenyls with the boiling point being estimated by Messiner’s method, but most of the predicted values were underestimated with large absolute average value of errors as the molecular weight increased.\(^6\) We have previously introduced the optimized exponent “\(m\)” into the modified Watson correlation to improve an accuracy in estimating \(P_{vp}\) values of organophosphorus pesticides possessing the P=S moiety.\(^7\) Furthermore, the number of possible hydrogen-bonding sites (NW) was found useful to improve estimated \(P_{vp}\) values, especially for the pesticides possessing the P-O moiety. Our method could correctly predict the log \(P_{vp}\) values of organophosphorus pesticides ranging from \(-5.0\) to 1.0.

In this report, the modified Watson method was improved in the similar procedures being taken for organophosphorus pesticides in order to estimate the \(P_{vp}\) values of carbamates. The \(P_{vp}\) value for each compound by the programmed temperature gas chromatography method (gradient GC method) was conveniently used as a reference due to its simplicity and reliability because the reported values are sometimes erroneous for compounds with very low vapor pressures.\(^2,8\)
MATERIALS AND METHODS

1. Measurement of Vapor Pressures

1.1 Chemicals

Carbamates and thiocarbamates were purchased from Wako Pure Chemical Industries (Osaka, Japan) and Kanto Chemical Company (Tokyo, Japan), and used without further purification. Di-n-buthylphthalate (DBP) and bis-2-ethylhexylphthalate (DEHP) in an analytical grade were purchased from Wako Pure Chemical Industries and used as internal standards in gas chromatographic analysis.

1.2 Gas chromatography

A Shimadzu 9AM gas chromatograph (GC) equipped with a flame ionization detector (FID) and an automatic injector system of Shimadzu AOC-9 was operated under the conditions described below. The carrier gas was helium at a flow rate of 30 ml/min, and the pressures of hydrogen and air were 0.6 and 0.5 kg/cm², respectively. A fused silica capillary column, Megabore DB-1, was used for analysis and the retention time of each peak was determined by a Shimadzu C-R5A Chromatopak. The peak was also identified using a Shimadzu QP-5000 gas chromatograph/mass spectrometry (GC-MS) being operated under the same conditions. According to the Donovan’s method, the column was initially maintained at 323 K for 2 min, increased at a rate of 10 K/min to the maximum temperature (563 K) and then held constant for 5 min. DBP and DEHP (1 g each) were dissolved in 200 ml of ethyl acetate to prepare the internal standard solution. Approximately 1 mg of a test substance was dissolved in about 1.5 ml of the internal standard solution and then the 4 μl aliquot was subjected to the GC analysis.

1.3 Estimation of Pvp,s values from the GC method

The Pvp,s value of a test substance at 298 K was estimated from its retention time in GC using the equation previously reported. The Pvp,s value of a solid substance obtained from this method is considered to be that in a subcooled liquid phase (Pvp,L), not in a solid one (Pvp,s). It is known that the Pvp,s value can be converted to Pvp,s by the following equation:

\[ \log (P_{vps}/P_{vp,L}) = -(S_f/R) (T_M/T - 1)/2.303 \]

where \( T_M \) is a melting point (in K), \( T \) is the temperature of interest (in K), and \( S_f/R \) is an entropy of fusion divided by the ideal gas constant which is equal to 6.8 in most cases. Since the figure of 6.8 is an averaged empirical value for compounds having short chains \( (n \leq 5) \), it may cause some error for that with a long chain. The \( S_f/R \) values for aldicarb, carbaryl, chlorpropham and methomyl are calculated by using the enthalpy values in literature to be 8.39, 7.03, 7.84 and 8.29, respectively, indicating the possibility of underestimation of the \( S_f/R \) value. Since the individual \( S_f/R \) value for each substance was not available in general, Pvp,s values for subcooled liquids obtained by the gradient GC method were conveniently used instead of those of solid in this study.

By the way, the GC method for methylcarbamate such as aldicarb, carbaryl, methomyl and oxamyl were found inadequate because of its low sensitivity or thermal decomposition of the carbamates. In the case of aldicarb, carbaryl and methomyl, no peak attributable to the parent was detected under the tested conditions, while peak of oxamyl was that of the corresponding oximino fragment. Therefore, they were excluded from the data set being used for optimization of the modified Watson method.

2. Method of Calculation of Pvp

In the modified Watson method, the Clausius-Clapeyron equation is integrated under the conditions that enthalpy of vaporization is dependent on temperature, which results in the following equation.

\[ \log P_{vp} = (\Delta H_{vap}/2.303 Z_b R T_b) \times (1 - (3 - 2 T_b) m) - 2m(3 - 2 T_b)^{m-1} \ln T_b \]

where \( \Delta H_{vap} \) is the enthalpy of vaporization (in J/mol) at the boiling point \( (T_b) \), \( Z_b \) is a compressibility factor, \( R \) is the gas constant, \( T_{vp} \) is \( T/T_b \) \( (T = 298 \text{ K}) \), \( m \) is an empirical constant. The \( \Delta H_{vap}/T_b \) value can be estimated by using the Fishtine’s method as expressed in the following equation:

\[ \Delta H_{vap}/T_b = K_f (8.75 + R \ln T_b) \]

where \( K_f \) values are provided for many chemical classes in the tabulated form reported by Grain. The boiling points \( (T_b) \) can be also estimated by the Meissner’s method as follows:

\[ T_b = (637 \times R_0^{1.47} + B)/P \]

where \( R_0 \) is a molar refraction, \( P \) is a parachor and \( B \) is a constant dependent on the functional group or moiety. Molar refraction is the constant defined in the Lorentz-Lorenz equation and is conveniently calculated using the Eisenlohr’s method where the characteristic values to each atom and bond are summed up. Parachor is a constitutive constant defined by Sugden between surface tension and liquid density and is known to be estimated in two ways using the Sugden’s or McGowan’s methods. In the former, the fragment value of parachor is defined for each atom and bond in a different chemical structure or a functional group. While the latter simply sums up the contribution to parachor from each atom, followed by subtraction of 19 times of the numerical number of bonds in the structure of a compound. McGowan’s parachor can be rapidly calculated, while Sugden’s one is known to be more accurate.
RESULTS AND DISCUSSION

1. Validation of Gradient GC Method

The $P_{vp}$ values of five carbamates measured by the gradient GC method were compared with the reliable values, as summarized in Table 1. The $P_{vp}$ values of chlorpropham and propoxur in a solid phase were adjusted to those in the subcooled phase by using the reported enthalpy and the default $S_f/R$ value (6.80), respectively.

The intrinsic error of log $P_{vp}$ values in the gradient GC method is generally considered to be within about 0.80.9) The $P_{vp}$ values of EPTC, propoxur and vernolate were in good agreement with the corresponding reported values and that of pebulate was within the range of the intrinsic error. Concerning chlorpropham, the gas saturation method, being the most reliable when the log $P_{vp}$ value of a compound is $<3.4^{21}$ afforded the log $P_{vp}$ value of $-1.56$, which was in good accordance with the measured log $P_{vp}$ value ($-1.24$) in the gradient GC method. The observed error in log $P_{vp}$ value is within 0.80 through these examination, indicating that the gradient GC method can be used as a convenient tool estimating the $P_{vp}$ values of carbamates in this study.

2. Optimization of the Original Modified Watson Method

The $P_{vp}$ values of 17 carbamates calculated by the original Watson method are listed in Table 2, together with those measured by the gradient GC method. When Sugden's parachor was used, the standard deviation, correlation coefficient and absolute average value of errors of the estimated log $P_{vp}$ values were 0.855, 0.780 and 0.84, respectively. In the case of McGowan’s parachor, the corresponding values were 0.814, 0.789 and 0.74, respectively. Most of the log $P_{vp}$ values were found to be overestimated by the original modified Watson method by considering the gradient GC method.

Incidentally, the most sensitive parameter was considered to be an empirical exponent “m” in the original modified Watson correlation (Equation 2) for enthalpy of vaporization, as previously reported. The optimum m values minimizing the difference in log $P_{vp}$ value against the gradient GC values were found to be 0.811 and 0.790 when Sugden’s and McGowan’s parachors were used, respectively. When the log $P_{vp}$ values of carbamates were calculated with the new m value using Sugden’s parachor, the standard deviation, calibration

Table 1 Comparison of vapor pressure between gradient GC method and literature values (Pa in log units).

<table>
<thead>
<tr>
<th>Compound</th>
<th>GC method (298 K)</th>
<th>Literature</th>
<th>Temp. (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorpropham</td>
<td>−1.24</td>
<td>−2.78</td>
<td>298</td>
</tr>
<tr>
<td>EPTC</td>
<td>0.31</td>
<td>0.03-0.67</td>
<td>293-298</td>
</tr>
<tr>
<td>Pebulate</td>
<td>−0.20</td>
<td>0.56-0.67</td>
<td>293-298</td>
</tr>
<tr>
<td>Propoxur</td>
<td>−0.99</td>
<td>−3.74−0.77</td>
<td>293</td>
</tr>
<tr>
<td>Vernolate</td>
<td>−0.16</td>
<td>−0.08-0.16</td>
<td>293-298</td>
</tr>
</tbody>
</table>

Table 2 Estimated vapor pressures by the original modified Watson method (Pa in log units).

<table>
<thead>
<tr>
<th>Compound</th>
<th>GC method</th>
<th>Sugden’s parachor</th>
<th>McGowan’s parachor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Estimated</td>
<td>Error</td>
</tr>
<tr>
<td>Bendiocarb</td>
<td>−1.36</td>
<td>−1.20</td>
<td>−0.16</td>
</tr>
<tr>
<td>Chlorpropham</td>
<td>−1.24</td>
<td>−0.79</td>
<td>−0.45</td>
</tr>
<tr>
<td>Cyclone</td>
<td>−1.12</td>
<td>0.12</td>
<td>−1.24</td>
</tr>
<tr>
<td>Diethofencarb</td>
<td>−2.58</td>
<td>−2.50</td>
<td>−0.08</td>
</tr>
<tr>
<td>EPTC</td>
<td>0.31</td>
<td>0.74</td>
<td>−0.43</td>
</tr>
<tr>
<td>Esprocarb</td>
<td>−2.54</td>
<td>−1.39</td>
<td>−1.15</td>
</tr>
<tr>
<td>Methiocarb</td>
<td>−2.51</td>
<td>−2.23</td>
<td>−0.28</td>
</tr>
<tr>
<td>Molinate</td>
<td>−0.56</td>
<td>0.51</td>
<td>−1.07</td>
</tr>
<tr>
<td>Xylycarb</td>
<td>−0.94</td>
<td>−0.23</td>
<td>−0.71</td>
</tr>
<tr>
<td>Orbencarb</td>
<td>−2.43</td>
<td>−1.01</td>
<td>−1.42</td>
</tr>
<tr>
<td>Pebulate</td>
<td>−0.20</td>
<td>0.46</td>
<td>−0.66</td>
</tr>
<tr>
<td>Pirimicarb</td>
<td>−2.13</td>
<td>−1.31</td>
<td>−0.82</td>
</tr>
<tr>
<td>Propoxur</td>
<td>−0.99</td>
<td>−0.65</td>
<td>−0.34</td>
</tr>
<tr>
<td>Swep</td>
<td>−1.68</td>
<td>−0.51</td>
<td>−1.17</td>
</tr>
<tr>
<td>Terbucarb</td>
<td>−2.59</td>
<td>−4.70</td>
<td>2.11</td>
</tr>
<tr>
<td>Thiobencarb</td>
<td>−2.52</td>
<td>−0.88</td>
<td>−1.64</td>
</tr>
<tr>
<td>XMC</td>
<td>−0.80</td>
<td>−0.23</td>
<td>−0.57</td>
</tr>
</tbody>
</table>

Average ± SD: −1.52 ± 0.93, 0.93 ± 1.32, 0.84, −1.03 ± 1.28, 0.74

a) Carbamate. b) Thiocarbamate. c) Average absolute value of errors.
coefficient and absolute average value of errors were slightly improved to be 0.724, 0.815 and 0.59, respectively, as evidenced by regression analysis. In the case of the McGowan's parachor, the corresponding values were 0.608, 0.852 and 0.51, respectively.

Since vaporization is a phenomenon in which a solute becomes free from the intermolecular force exerted by neighboring molecules, it is most likely that formation of hydrogen bond plays a great role in making the intermolecular force stronger. In the case of carbamates and thiocarbamates, nitrogen and oxygen atoms in the N(H)COO and N(H)COS moieties are most likely to act as a hydrogen-bond acceptor and hydrogen atom does as a donor, indicating the significant contribution of hydrogen bond to the $P_{vp}$ values. Since we have successfully introduced the NW parameter which are summation of the number of donor and acceptor sites forming hydrogen bonds in estimating $P_{vp}$ values of organophosphorus pesticides (P=O compounds), this parameter was also applied to carbamates. The estimated $P_{vp}$ values by the modified Watson method with the optimum $m$ values and NW parameters were subjected to the regression analysis with the F-test against $P_{vp}$ values measured by the gradient GC method. Although carbamates used in this analysis are classified in RNHCOOR', RR'NCOOR'' and RR'NCOSR'' (R, R' and R'': aryl or alkyl), the NW values have not been defined yet. The NW values were newly defined to be 3, 2 and 2, respectively, by taking account of NW(RNHR') = 2, NW(RR'NR'') = 1 and NW(RCOR'') = 1.22. The two equations obtained were as follows:

With Sugden's parachor
\[
\log (P_{vp,GC}) = 0.672 \pm 0.095 \times \log (P_{vp,est}) - 0.286 \pm 0.097 \times NW + 0.361 \pm 0.350
\]
SD = 0.453, $R = 0.891$, $F(2,16) = 26.9$

With McGowan's parachor
\[
\log (P_{vp,GC}) = 0.734 \pm 0.093 \times \log (P_{vp,est}) - 0.251 \pm 0.088 \times NW + 0.410 \pm 0.322
\]
SD = 0.415, $R = 0.909$, $F(2,16) = 33.4$

where $log (P_{vp,GC})$ and $log (P_{vp,est})$ are the vapor pressures in log units measured by the gradient GC method and estimated by the modified Watson method with the optimum $m$ values, respectively. The standard deviations, correlation coefficients and absolute average value of errors between gradient GC method and estimated values for each step were summarized in Table 3.

Both the higher correlation coefficient and the F-test justified the introduction of NW with 98.7% certitude. The negative sign of the regression coefficient of NW in Equations (5) and (6) implies that the vapor pressure is the most likely to be reduced by possible formation of hydrogen bonds, coinciding with our concept.

The log $P_{vp}$ values estimated by Equations (5) and (6) are shown in Table 4. For the carbamates being tested, the standard deviations, regression coefficients and absolute average value of errors between gradient GC and estimated values were 0.399, 0.882 and 0.35 using the Sugden's parachor and 0.367, 0.905 and 0.32 using the McGowan's parachor.

![Fig. 1 Vapor pressures of carbamate pesticides (gradient GC method vs. estimated values).](image)

Table 3 The standard deviations, correlation coefficients and absolute average value of errors through the optimization procedure.

<table>
<thead>
<tr>
<th>Method</th>
<th>Standard Deviation</th>
<th>Correlation Coefficient</th>
<th>Absolute average value of errors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original modified Watson method</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sugden's parachor</td>
<td>0.855</td>
<td>0.780</td>
<td>0.84</td>
</tr>
<tr>
<td>McGowan's parachor</td>
<td>0.814</td>
<td>0.789</td>
<td>0.74</td>
</tr>
<tr>
<td>After applying optimum $m$ value</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sugden's parachor</td>
<td>0.724</td>
<td>0.815</td>
<td>0.59</td>
</tr>
<tr>
<td>McGowan's parachor</td>
<td>0.608</td>
<td>0.852</td>
<td>0.51</td>
</tr>
<tr>
<td>After applying NW value with an optimum $m$ value</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sugden's parachor</td>
<td>0.399</td>
<td>0.882</td>
<td>0.35</td>
</tr>
<tr>
<td>McGowan's parachor</td>
<td>0.367</td>
<td>0.905</td>
<td>0.32</td>
</tr>
</tbody>
</table>
McGowan’s parachor, respectively. Although the maximal errors in the log $P_{vp}$ values between the gradient GC method and newly derived equations were 0.82-0.88 for EPTC, the errors were considered acceptable if the deviation and inherent errors in the gradient GC method were taken into account.

In summary, the optimum $m$ values and correction by the NW parameters in Equations (5) and (6) were practically useful to estimate the vapor pressures for carbamates.

### 3. Validation of the Newly Modified Watson Method

Applicability of the newly modified Watson method expressed in Equations (5) and (6) was examined for nine carbamates which were not utilized in the regression analysis. The results of calculation were summarized in Table 5. For benfuracarb, the NW value was taken as 4 based on $\text{NW}(\text{RR’NCOOR’})=2$, $\text{NW}(\text{R}_3\text{N})=1$ and $\text{NW}(\text{RCOR’})=1$. The standard deviations, correlation coefficients and average absolute value of errors between gradient GC and estimated values by new method using Sugden’s and McGowan’s parachor were 0.477-0.499, 0.968-0.970 and 0.44, respectively. These results show that the new method can estimate $P_{vp}$ values of carbamates within one log unit of the error.

The new method was also applied to carbamates whose $P_{vp}$ values could not be measured by the gradient GC method (Table 6). For aldicarb, methomyl and oxamyl, the NW values of 4, 4 and 6, respectively, were used by taking account of $\text{NW} (\text{RNHCOOR’})=3$, $\text{NW}(\text{R}_3\text{N})=1$ and $\text{NW}(\text{RCOR’})=1$. Estimated values were found to be within the range of reported values being corrected using $S_f/R$ values or inherent error of gradient GC method. Since the reported log $P_{vp}$ values exhibit a broad range (2.08-2.98), its order among the three oxime carbamates can not be easily estimated. Incidentally, the molecular weight of aldicarb, methomyl and oxamyl are 190.3, 162.2 and 219.3 and their melting points are 371-373, 351-352 and 381-383 K, respectively. Judging from the molecular weight and the melting point, the log $P_{vp}$ values are considered to be in order of oxamyl < aldicarb < methomyl, which is in agreement with our estimation.

### CONCLUSION

The equations newly derived from the modified Watson method are based solely on the chemical structure and applicable to carbamates having various functional groups or bond types without any measurement tech-
The new method could estimate vapor pressures for carbamates ranging from 10^{-5} to 10^1 Pa at 298 K within an allowable deviation almost below a factor of one log unit as compared with those of the gradient GC method.

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化学構造のカーバメート系およびチオカーバメート系農薬の蒸気圧を、化学構造のみから推算する方法を開発した。

各農薬の蒸気圧として、Donovan（1996）のガスクロ法によって算出した値を用い、現行のModified Watson法の推算値と比較したが、ほとんどの農薬について推算値の方が高価を示した。そこで、Modified Watson法の定数$m$の最適化を行った結果、Sugden's parachorを使用した場合$m=0.811$、McGowan's parachorの場合$m=0.790$が最適であった。さらに、蒸気圧にとって分子間に形成される水素結合の影響が重要なファクターであることから、最適化したModified Watson法に分子構造中の水素結合部位数（NW）の概念を導入した結果、分析（ガスクロ法）による蒸気圧値との差がさらに著しく減少した。

最適化過程に使用していない農薬を用いて、本法の検証を行ったところ、ガスクロ法の誤差範囲内で文献値とほぼ一致した。本法により、カーバメート系およびチオカーバメート系農薬について、分析を必要とせず、化学構造のみから$10^{-3} \sim 10^5$ Paの範囲の蒸気圧を推算できることが示唆された。