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Article

A Simple Method to Evaluate, Correlate and Predict Boiling and Flash Points of Alkynes

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Pontos de ebulição (T_B) de alcinos acíclicos são preditos a partir de seus números de ponto de ebulição (Y_{BP}) com a relação: $T_B(K) = -16,802Y_{BP}^{2/3} + 337,377Y_{BP}^{1/3} - 437,883$. Os valores de Y_{BP}, por sua vez, são calculados a partir da estrutura dos compostos utilizando a equação: $Y_{BP} = 1,726 + A_i + 2,779C + 1,716M_3 + 1,564M + 4,204E_3 + 3,905E + 5,007P - 0,329D + 0,241G + 0,479V + 0,967T + 0,574S$. O valor de A_i depende do padrão de substituição do alcino e o restante da equação é o mesmo relatado anteriormente para alcanos. Para um conjunto de dados de 76 alcinos acíclicos, a correlação entre os valores de T_B previstos e da literatura apresentou um desvio médio absoluto de 1,46K com um valor de R^2 de 0,999. Além disso, os valores de Y_{BP} também podem ser utilizados para prever os pontos de fulgor dos alcinos.

Boiling points (T_B) of acyclic alkynes are predicted from their boiling point numbers (Y_{BP}) with the relationship $T_B(K) = -16.802Y_{BP}^{2/3} + 337.377Y_{BP}^{1/3} - 437.883$. In turn, Y_{BP} values are calculated from structure using the equation $Y_{BP} = 1.726 + A_i + 2.779C + 1.716M_3 + 1.564M + 4.204E_3 + 3.905E + 5.007P - 0.329D + 0.241G + 0.479V + 0.967T + 0.574S$. Here A_i depends on the substitution pattern of the alkyne and the remainder of the equation is the same as that reported earlier for alkanes. For a data set consisting of 76 acyclic alkynes, the correlation of predicted and literature T_B values had an average absolute deviation of 1.46 K, and the R^2 of the correlation was 0.999. In addition, the calculated Y_{BP} values can be used to predict the flash points of alkynes.

Keywords: alkynes, boiling point, flash point, correlation, prediction

Introduction

Boiling point (T_B) is arguably the most important physical property of an organic compound that is liquid at room temperature. Chemists intuitively assume a direct relationship between molecular structure and the boiling point of a substance, but expressing this relationship with a simple mathematical formula is challenging. Therefore, methods to predict T_B values continue to attract wide interest.[1] As is often the case in chemistry, however, it is usually necessary to choose between simple relationships with limited accuracy and more complex methods that can be more accurate.[2]

The prediction of boiling point from molecular structure is complicated by the fact that the T_B values of homologous organic compounds increase nonlinearly with the incremental addition of repeat units. For example,

Figure 1 shows the curvature when boiling points (•) of linear 1-alkynes, from 1-hexyne to 1-triacontyne, are plotted against the number of carbon atoms in the chain. For this reason, methods to predict boiling points directly from simple structure counts can be reasonably accurate over the narrow range of molecular sizes for which the methods were developed, but they become increasingly inaccurate as the structures become larger. Therefore, most of the recently reported methods for calculating boiling points incorporate a series of topological functions or theoretical parameters that, taken together, can yield curvature when predicted boiling points are plotted against chain length.

Recently we introduced a new approach to physical property prediction. The available experimental values of a property of interest are first transformed into units of a new parameter having values that vary linearly with the number of structural units in a series of homologous compounds. Then a relationship is developed to calculate values of the new parameter from structure. Finally, the calculated
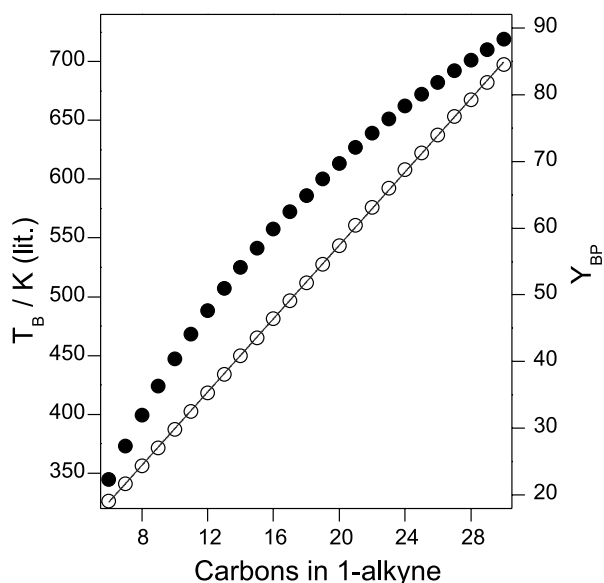
Figure 1. Nonlinear relationship of literature T_B values (●, left axis) and linear relationship of Y_{BP} values (○, right axis) with the number of carbon atoms in a series of unbranched 1-alkynes ranging from 1-hexyne to 1-triacontyne. The solid line shows the linear correlation ($R^2 = 0.9999$) of the Y_{BP} values.

values of the new parameter are used to predict values of the physical property of interest for other homologous compounds. For boiling points, the new parameter is the boiling point number, Y_{BP}. Values of T_B relate to values of Y_{BP} *via* equation 1, where a = −16.802, b = 337.377, and c = −437.833.[3] As shown in Figure 1, there is an excellent correlation of Y_{BP} values calculated in this way with the number of carbon atoms in the unbranched 1-alkynes.

$$Y_{BP} = \left[\frac{-b + \sqrt{b^2 - 4a(c - T_B)}}{2a} \right]^3 \qquad (1)$$

Our initial investigation of the relationship between Y_{BP} values and molecular structure was carried out with acyclic alkanes (this work was based on an early report by Kinney,[4] who introduced the concept of a boiling point number, Y, as a measure of T_B values). Their Y_{BP} values could be predicted quite accurately from molecular structure, as is shown in equation 2.[3]

$Y_{BP} = 1.726 + 2.779C + 1.716M_3 + 1.564M + 4.204E_3 + 3.905E + 5.007P − 0.329D + 0.241G + 0.479V + 0.967T + 0.574S \qquad (2)$

Here, C is the number of carbon atoms in the longest chain, M_3 is the number of methyl substituents on carbon 3 of this chain (counting from either end), M is the number of methyl substituents elsewhere on the chain, E_3 and E are the

number of corresponding ethyl substituents, P is the number of propyl substituents, D is the number of 2,2-dimethyl groupings (counting from either end), G is the number of geminal substitutions at other positions, V is the number of vicinal alkyl relationships, T is the number of instances of two methyl substituents on both carbons one and three of a three-carbon segment of the parent chain, and S is the square of the ratio of total number of carbons to the number of carbons in the longest chain. This approach gave a correlation of experimental and predicted boiling points having $R^2 = 0.999$ for 198 acyclic alkanes containing from six to 30 carbons.[3]

Based on the success of this approach for alkanes, we have begun to explore the prediction of T_B values of other organic compounds. Recently we reported excellent correlations for the boiling points of alkenes[5] and alkylbenzenes.[6] Here we extend this approach to the calculation of boiling points of acyclic alkynes. A prediction method is needed for this class of compounds because surprisingly few experimental T_B values are available for alkynes. The method we report here not only provides a convenient boiling point prediction capability, but it also can be used to predict the flash points of the alkynes.

Method

We compiled a data set containing the literature boiling points for 66 linear and 10 branched acyclic alkynes containing from six to 30 carbon atoms in the main chain (the alkynes, their boiling points, flash points, and literature references are provided in the Supplementary Information).

Next we modified equation 2, which was originally developed for alkanes, so that the Y_{BP} values of alkynes could also be calculated directly from molecular structure. In doing so, we wished to change equation 2 as little as possible, because the structural parameters responsible for intermolecular attractions of alkanes should influence the intermolecular attractions of the aliphatic portions of alkynes in the same way. Thus we modified equation 2 only by adding the parameter A_i, which reflects the difference in intermolecular attraction resulting from the substitution of a –C≡C– unit for a CH_3–CH_2– or –CH_2–CH_2– segment at different locations along the carbon chain of an alkane. The resulting expression is shown in equation 3.

$Y_{BP} = 1.726 + A_i + 2.779C + 1.716M_3 + 1.564M + 4.204E_3 + 3.905E + 5.007P − 0.329D + 0.241G + 0.479V + 0.967T + 0.574S \qquad (3)$

Other than the term A_i, the parameters and coefficients in equation 3 are identical to those in equation 2. However,

we did make a slight change in the interpretation of one parameter. For steric reasons, a methyl substituent on C3 of a 1-alkyne was counted as M instead of M_3. A similar interpretation of the M_3 parameter was made for the alkenes.[5] We should note that, for lack of literature values, our data set does not include compounds with ethyl or propyl groups, nor do any structures have V, G, or T substitution patterns. We have retained those parameters in equation 3, however, so that it can be used to predict boiling points of compounds having those structural features.

To evaluate this approach, we used initial guesses for the A_i values associated with different patterns of acetylenic substitution in equation 3 to estimate Y_{BP} values of the alkynes. Using the Solver add-in of Microsoft Excel, we then determined the values of A_i that produced the lowest average absolute deviation (AAD) between the Y_{BP} values determined from experimental boiling points with equation 1 and those predicted from molecular structure using equation 3.

Results and Discussion

The best values of A_i for different alkyne bonding patterns are shown in Table 1.

Table 1. A_i values for use in equation 3

Alkyne position	A_i
1-alkyne	−0.324
2-alkyne	1.261
3-alkyne	0.298
4- or higher alkyne	0.211

Although these values for A_i are empirical, they are chemically reasonable. They can be rationalized as the net effect of the loss of dispersion resulting from the removal of four hydrogen atoms from the corresponding alkane and the increase in intermolecular attraction made possible by the greater linearity of a structure with a carbon-carbon triple bond. Only three carbons are necessarily collinear in a 1-alkyne, so the overall effect is a slight decrease in intermolecular attraction. A 2-alkyne has four collinear carbon atoms at one end of the chain, so intermolecular attraction is much greater than in the corresponding alkane. A 3-alkyne also has four collinear carbon atoms, but now there are non-collinear segments at each end of that four-carbon segment. As a result, the total increase in intermolecular attraction is less than for a 2-alkyne, so the A_i value for a 3-alkyne is less positive than that of

a 2-alkyne. The non-collinear segments are even longer for a 4- or higher alkyne, so the A_i value for a 4-alkyne is smaller still. An even better correlation between literature and predicted values can be obtained by use of separate parameters for 4-alkynes and 5- or higher alkynes. We judged the improvement insufficient to justify addition of another parameter, however.

As an example of the application of equation 3, consider the calculation of Y_{BP} for 2-methyl-3-octyne. This is a 3-alkyne, so the A_i value is 0.298 from Table 1. There is one methyl substituent on C2, so M is 1. The longest chain has eight carbon atoms, and the total number of carbons in the molecule is nine. Therefore, $S = (9/8)^2 = 1.27$. The M_3, E, E_3, P, D, G, V, and T parameters are all 0. For this compound, therefore, $Y_{BP} = 1.726 + 0.298 + (8 \times 2.779) + 1.564 + (1.27 \times 0.574) = 26.55$. The Y_{BP} value calculated from equation 1 is 26.48.

The Y_{BP} values of the other alkynes were calculated from equation 3 in the same way, and these Y_{BP} values were then used to predict T_B values with equation 4.[3] This produced a very good correlation of literature and predicted boiling points, as is shown in Figure 2. Here $R^2 = 0.999$, the standard error is 1.99 K, and the AAD between literature and predicted T_B values is 1.46 K.

$$T_B(K) = -16.802 Y_{BP}^{2/3} + 337.377 Y_{BP}^{1/3} - 437.883 \qquad (4)$$

The correlation presented here is more accurate than any alkyne boiling point method previously reported. The
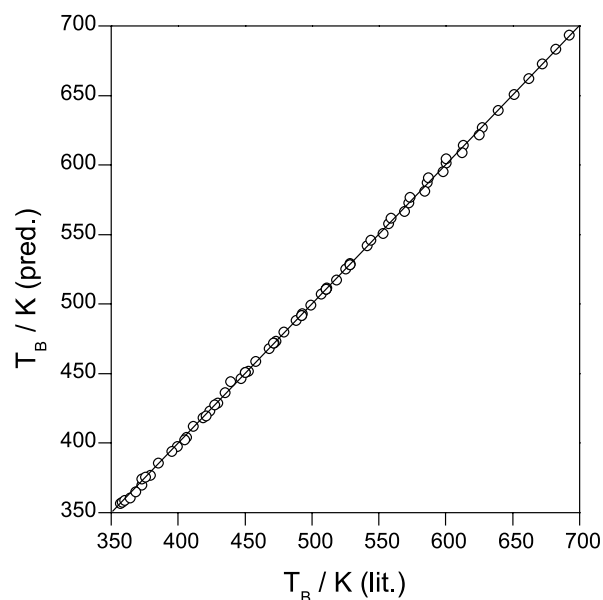

Figure 2. Correlation of literature boiling points of 76 linear and branched acyclic alkynes with predicted values based on Y_{BP} values calculated from structure *via* equation 3. The diagonal line represents perfect correlation of literature T_B values. For better visibility, the data points are sized to indicate twice the standard error of the correlation.

Joback-Reid approach[7] gave an AAD of 27.1 K for the 76 alkynes in our data set. A group contribution method for non-electrolytes, which was based on counts of molecular fragments and a steric factor plus consideration of group interactions, gave an AAD of 3.01 K for a data set having 25 alkynes.[8] Another method used a six-variable linear model incorporating molecular connectivity and computed values of electron density surfaces to predict the boiling points of hydrocarbons. It gave an AAD of 6.29 K for a set of 12 acyclic alkynes containing up to eight carbon atoms.[9] A method for predicting boiling points of hydrocarbons in general, which incorporated group contributions and topological parameters, produced an AAD of 3.59 K for a group of 47 alkynes.[10] Thus, the method we report is significantly more accurate than any of these other methods, even though it was evaluated on a much larger data set. Additionally, the correlation reported here is based directly on structure counts, so it does not require specialized software for implementation.

Not only does the method presented here allow the prediction of boiling points for compounds that have not yet been characterized, but it also can be used to evaluate literature boiling point data. As shown in Figure 3, the reported boiling point of 2-tetradecyne (525.7 K)[11] is qualitatively inconsistent with the boiling points of homologous compounds. For this reason, we had concluded that the reported T_B value of 2-tetradecyne is likely to be in error and excluded this compound from the data set. That assessment is validated by the Y_{BP} values shown in Figure 3. There is no obvious chemical reason why the Y_{BP} value of 2-tetradecyne (indicated with the symbol ×) should deviate from the excellent linear trend exhibited by so many homologous compounds, so we suggest that the experimental boiling point of 2-tetradecyne be redetermined.[12]

The results of the present study can be extended to the prediction of flash points of alkynes. The flash point (T_{FP}) of a liquid is the lowest temperature at which the mixture of vapor and air above the substance can be ignited. For this reason, flash points are the standard measure of the fire hazard associated with the storage, transport, and use of flammable compounds. Experimental flash points are often unavailable for alkynes, however, and we could locate experimental T_{FP} values for only about half of the alkynes in our data set.

Recently we introduced the flash point number, N_{FP}, as a new measure of the flammability of organic liquids. The relationship reported between flash points and N_{FP} values is shown in equation 5.[13]

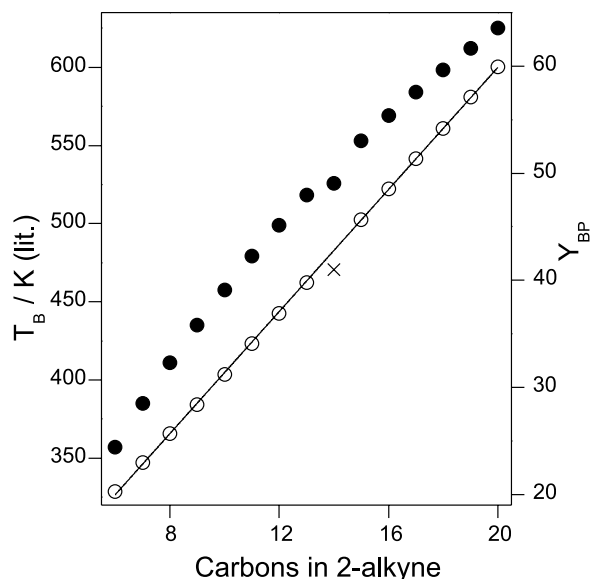$$T_{FP}(K) = 23.369 N_{FP}^{2/3} + 20.010 N_{FP}^{1/3} + 31.901 \qquad (5)$$

Figure 3. Nonlinear relationship of literature T_B values (●, left axis) and linear relationship of Y_{BP} values (○, right axis) with the number of carbon atoms in a series of unbranched 2-alkynes ranging from 2-hexyne to 2-icosyne. The solid line shows the linear correlation ($R^2 = 0.9999$) of the Y_{BP} values for all of the compounds except 2-tetradecyne (×).

We also demonstrated that there is a strong relationship between the N_{FP} and Y_{BP} values of hydrocarbons, as shown in equation 6.[14] Here D is the number of olefinic double bonds in the structure, T is the number of triple bonds, and B is the number of aromatic rings.

$$N_{FP} = 0.987 Y_{BP} + 0.176D + 0.687T + 0.712B - 0.176 \quad (6)$$

For monoalkynes, T is 1, and both D and B are 0, so equation 6 reduces to equation 7.

$$N_{FP} = 0.987 Y_{BP} + 0.511 \qquad\qquad (7)$$

We used equation 7 and Y_{BP} values predicted with equation 3 to calculate the N_{FP} values of the compounds in our data set. Then we used those N_{FP} values in equation 5 to predict their flash points. There was a good correlation (Figure 4) between these predicted T_{FP} values and the reported T_{FP} values for 39 alkynes boiling below 550 K for which reported T_{FP} values were found. Equation 5 was developed with a data set of linear and branched alkanes having boiling points of 589 K or lower and flash points of 438 K or less.[13] In the alkenes study,[5] there was an increasing deviation between reported and predicted T_{FP} values for compounds that boil above 550 K. A similar pattern was observed in the current study, so the limit of applicability of equation 5 seems to be T_B values below 550 K. Further work will be necessary to determine a more accurate correlation of N_{FP} and T_{FP} values for higher boiling

alkynes. The R^2 of the correlation was 0.995, and the AAD between literature and predicted values was 2.51 K. This result compares favorably with those of other methods for predicting hydrocarbon flash points from structure, which give AADs of 6-12 K.[14,15] Thus, the Y_{BP} values calculated from equation 3 can be used to predict the flash points of acyclic alkynes more accurately than with previous methods.
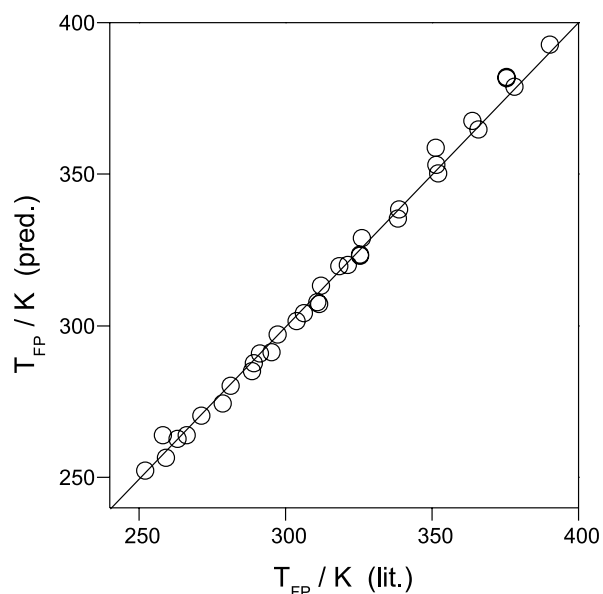

Figure 4. Correlation of reported flash points of 39 linear and branched acyclic alkynes with T_{FP} values calculated using Y_{BP} values predicted with equation 3. The diagonal line represents a perfect correlation of literature and predicted values, and the size of the data points indicates the standard error in the correlation.

Conclusions

The boiling point prediction method presented here is not only very easy to apply to acyclic alkynes, but it is also more accurate than previous methods. Comparison of reported alkyne boiling points with those predicted using equation 4 offers a simple means to identify literature T_B values that should be redetermined. In addition, the Y_{BP} values calculated with equation 3 are useful for the prediction of the flash points of alkynes. Efforts to develop similar correlations for other families of organic compounds are underway.

Supplementary Information

The data set of alkynes along with their literature boiling points, Y_{BP} values, counts of the structural parameters used in equation 3, reported flash points, literature references, and predicted T_{FP} values are provided in the Supplementary Information. This material is available free of charge at http://jbcs.sbq.org.br as a PDF file.

Acknowledgments

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