Prediction of Vapour Pressure and Boiling Points of Aliphatic Compounds

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The possibility of predicting the vapour pressure and boiling points of aliphatic compounds by methods based on the linear free energy relationship has been established.

We have shown previously[1,2] that substituent (R) variation in aromatic structures results in proportional changes in the free energy of evaporation ($G^0_{\rm ev}$) and the saturated vapour pressure (p) of liquid compounds, related by the expression:

$$\lg p = -G^0_{\rm ev}/2.3RT$$

In the same work we also introduced a scale of new structural characteristics, $\xi_{\rm R}$ constants, reflecting the contribution of R to $G^0_{\rm ev}$ of aromatic compounds. The $\xi_{\rm R}$ constants were calculated from $G^0_{\rm ev}$ for monosubstituted benzenes chosen as a standard series:

$$-(G^{0,{\rm C_6H_5R}}_{\rm ev} - G^{0,{\rm C_6H_6}}_{\rm ev})/2.3RT = \xi_{\rm R}$$

Using the linear free energy relationship (LFER) has allowed us to estimate quantitatively the values of p, $G^0_{\rm ev}$ and boiling points ($T_{\rm b}$) for a wide range of aromatic compounds based on their structural formulae and the data sets required to calculate the basic correlations of the types:

$$\lg p^{\rm R} - \lg p^{\rm H} = -(G^{0,{\rm R}}_{\rm ev} - G^{0,{\rm H}}_{\rm ev})/2.3RT = æ\xi_{\rm R} \qquad (1)$$

$$T^{\rm R}_{\rm b} = T^{\rm H}_{\rm b}(1 + a\xi_{\rm R})/(1 + b\xi_{\rm R}) \qquad (2)$$

where the indices R and H refer to the substituted and unsubstituted compounds, respectively, and æ, a and b are constants characterising the given series of compounds.[1–3]

Aromatic compounds present the simplest model for studying structure–property relationships. However, the laws characterising them within the scope of the LFER principle may not necessarily be expanded for describing compounds of the aliphatic series. Meanwhile, the elaboration of methods for predicting p, $G^0_{\rm ev}$ and $T_{\rm b}$ for these compounds seems to be an urgent problem.

Therefore, we have made an attempt to describe these parameters for aliphatic compounds based on the same scale of $\xi_{\rm R}$ constants. For this purpose, we calculated $-G^0_{\rm ev}/2.3RT$ from the literature data[4,5] for 1-monosubstituted hexanes and cyclohexanes at 293 K, similarly to our previous work.[1,2] The set of compounds analysed was restricted by the availability of $\xi_{\rm R}$ constants already tabulated.

An analysis of the calculated values of $-G^0_{\rm ev}/2.3RT$ indicates that they are proportional to $\xi_{\rm R}$ (Fig. 1), which is confirmed by the results of a mathematical treatment of the data. The dependencies obtained are approximated by linear equations:

$$\text{hexanes:}\quad -G^{0,{\rm R}}_{\rm ev}/2.3RT = 2.08 + 1.00\xi_{\rm R},\quad n = 52,\ r = 0.998,\ s = 0.19 \qquad (3)$$

$$\text{cyclohexanes:}\quad -G^{0,{\rm R}}_{\rm ev}/2.3RT = 1.43 + 0.77\xi_{\rm R},\quad n = 45,\ r = 0.996,\ s = 0.24 \qquad (4)$$

where n is the number of compounds and r is the correlation coefficient. According to ref. 6, these approximations are "excellent". The standard deviations (s) for equations (3) and (4) do not exceed 1.7% and 2.6% of the $-G^0_{\rm ev}/2.3RT$ range, while the free members of these equations are close to the corresponding $\lg p$ for hexane (2.02) and cyclohexane (1.56).

In addition, the use of $\xi_{\rm R}$ constants provides high precision in describing the $T_{\rm b}$ of aliphatic compounds. This is demonstrated by equations (5) and (6):

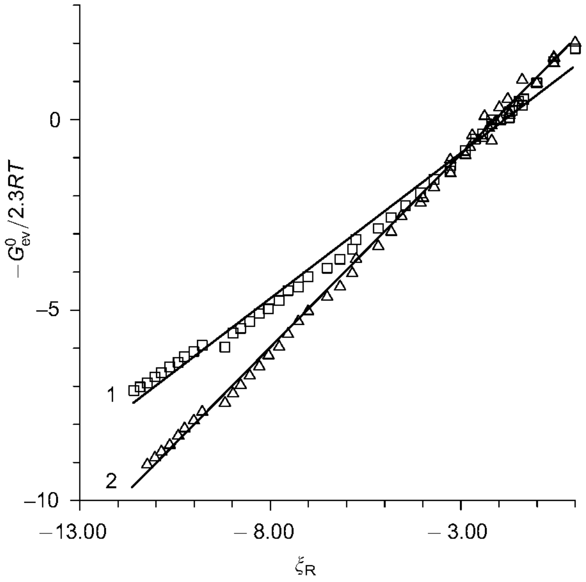

Fig. 1 Dependencies of $-G^{0,{\rm R}}_{\rm ev}/2.3RT$ on $\xi_{\rm R}$ for 1-monosubstituted hexanes (1) and cyclohexanes (2) at 293 K.

hexanes:

$$T^{\rm R}_{\rm b} = 332.39(1 - 18.34 \times 10^{-2}\xi_{\rm R})/(1 - 25.81 \times 10^{-3}\xi_{\rm R}),\quad n = 52,\ s = 12.48 \qquad (5)$$

cyclohexanes:

$$T^{\rm R}_{\rm b} = 332.09(1 - 24.83 \times 10^{-2}\xi_{\rm R})/(1 - 49.22 \times 10^{-3}\xi_{\rm R}),\quad n = 45,\ s = 12.05 \qquad (6)$$

It is important that the small values of b in these equations make it possible, as in the case of the aromatic series,[3] to approximate $T_{\rm b}$ of aliphatic compounds by simpler equations of the type:

$$T^{\rm R}_{\rm b} = T^{\rm H}_{\rm b} + c\xi_{\rm R} \qquad (7)$$

without substantial errors. In fact, the same data sets are "excellently" described by linear equations:

hexanes:

$$T^{\rm R}_{\rm b} = 360.81 - 40.49\xi_{\rm R} \quad n = 52,\ r = 0.994,\ s = 15.01 \qquad (8)$$

cyclohexanes:

$$T^{\rm R}_{\rm b} = 378.64 - 40.26\xi_{\rm R} \quad n = 45,\ r = 0.996,\ s = 13.76 \qquad (9)$$

This fact suggests that $G^0_{\rm ev}$ (or p for liquid compounds) and $T_{\rm b}$ of aliphatic compounds obey the LFER principle in the same way as for aromatic compounds, and that the $\xi_{\rm R}$ scale of constants is applicable within this series of compounds and allows the prediction of the above values by correlation methods.

However, the practical use of correlations such as (1), (2) or (7) requires that the data relating to the basic set be recalculated to equal conditions. For example, the quantitative estimation of p requires data recalculated to equal temperature, while the prediction of T_b requires data recalculated to equal pressure. Unfortunately, handbooks usually contain p or T_b measured under different conditions. Nevertheless, the more complex two-parameter correlations containing cross-terms again allow one to obtain equations with a high predictive ability in this case. This approach is based on the fact that the $\lg p - 1/T$ and $\lg P - \xi_R$ dependencies are simultaneously linear. This allows a polylinear representation of $\lg p$ as a function of two variables:[7]

$$\lg p_T^R = A + B/T + C\xi_R + D\xi_R/T \tag{10}$$

where A, B, C and D are constants. One can easily see that dependencies of this type do not require bringing of the basic data set to unified temperatures and pressures.

In order to verify the validity of equation (10), the data on T_b for monosubstituted hexanes and cyclohexanes obtained at 1, 10, 30 (or 40), 100, 400 and 760 mmHg[4] were fitted by dependencies of this type without any additional mathematical treatment.

hexanes:

$$\lg p_T^R = 8.07 - 1731.3/T - 0.18\xi_R + 349.2\xi_R/T, \quad n = 312, \ r = 0.989, \ s = 0.14 \tag{11}$$

cyclohexanes:

$$\lg p_T^R = 7.41 - 1646.1/T - 0.15\xi_R + 295.62\xi_R/T, \quad n = 235, \ r = 0.994, \ s = 0.11 \tag{12}$$

The equations obtained adequately describe the data, which is shown by r values close to 1 and small s values. This confirms the validity of equation (10) and allows us to use correlation dependencies derived from it for predicting the p values of organic compounds at various temperatures and to estimate qualitatively the T_b values corresponding to the desired p values.

It is important that the basic correlation dependencies of type (10) can be calculated based on accessible T_b data for organic compounds, if at least a fraction of the measurements have been carried out at pressures other than atmospheric pressure. For example, the mathematical treatment of T_b for monosubstituted cyclohexanes[8] affords an equation which is similar to equation (12) derived from a broad set of high precision data:

$$\lg p_T^R = 7.39 - 1642.0/T - 0.35\xi_R + 356.8\xi_R/T, \quad n = 36, \ r = 0.986, \ s = 0.14 \tag{13}$$

The differences between the coefficients of these equations do not exceed the confidence intervals for eqn. (13), which amount to 0.98, 381.5, 0.43 and 171.9 for A, B, C and D, respectively, at the 95% confidence level.

It should be noted that the methods developed in this communication for a quantitative estimation of p for aliphatic compounds at different temperatures (or their T_b at different pressures) can also be successfully used for other classes of compounds whose p values can be described based on the LFER. In general, the possibility of a simultaneous account both of the structural parameters of R and the temperature renders our approach flexible and makes it possible to use it in practice to predict the properties of organic compounds, including those not yet synthesised, based on their structural formulae and the data set necessary for calculating the basic correlation.

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