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A Correlation between Boiling Points and Refractive Indices of Organic Compounds: A Possible Role of Fluorine Atoms in Intermolecular Interactions

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Correlations between boiling points and refractive indices of halogenated organic compounds are described. We note fair to excellent linear relationships between the boiling points of the compounds and the refractive indices.

The importance of an estimating method for boiling points needs no restatement.[1] To date, many empirical and theoretical methods had been proposed. Among them, one of the most popular and semi-quantitative methods would be the principle that boiling points of structurally similar compounds mainly depend on their molecular weights. Actually, halogenated organic compounds attain higher boiling points along with their higher molecular weights, except for some fluorinated compounds.[2] When the boiling points of some halogenated acetic acids were correlated with molecular weights as shown in Fig. 1, we found a gradual curved correlation between molecular weights and boiling points except for di- and trifluoroacetic acids. Monofluoroacetic acid boils at the temperature just on this correlating curve (bp 438 K), while difluoroacetic acid (bp 407 K) and tri-fluoroacetic acid (bp 346 K) boil at notably lower temperatures than those expected from the curve.[2] Such curious boiling points of fluorinated acetic acids had been attributed to the hydrogen bonding of their methyl groups.[3] However, this explanation did not work to explain the lower boiling point of trifluoroacetic acid being much lower than that of nonfluorinated acetic acid (bp 391 K).

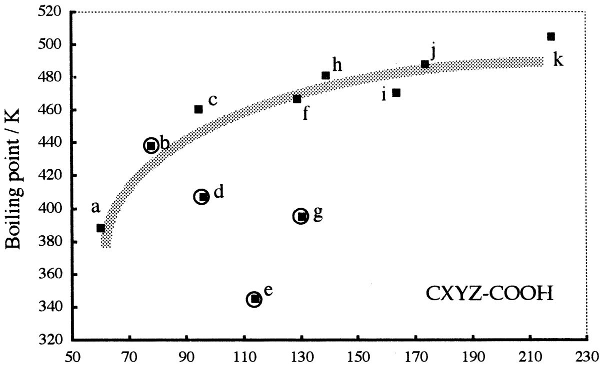

Fig. 1. Boiling points of halogenated acetic acids as a function of molecular weight. Double circles are fluorinated acetic acids. a) acetic acid, b) fluoroacetic acid, c) chloroacetic acid, d) difluoroacetic acid, e) trifluoroacetic acid, f) dichloroacetic acid, g) chlorodifluoroacetic acid, h) bromoacetic acid, i) trichloroacetic acid, j) bromochloroacetic acid, k) dibromoacetic acid.

Trouton's rule suggests that the boiling points are depending on latent heats of vaporization, the energy of molecular interaction.[4] Thus, we have to reconsider the interaction energy for better understanding of the boiling point, especially of fluorinated organic molecules.

Instead of conventional classifications, it would be reasonable to classify the intermolecular forces[4] into three categories based on their origins. The first is the forces caused by the electronic polarization, such as London dispersion (electronic polarization–electronic polarization) and Debye interaction (dipole–dipole-induced electronic polarization). The second is the forces caused by the electrostatic charges and/or the dipoles of the molecule, which is based on the molecular structure and is independent from electronic polarizability. And the last category is the forces caused by exchange of elemental particles, such as an electron and a proton, and is based mainly on orbitals.

In the series of acetic acids, the interactions due to the second and the last categories should be enhanced by fluorination, while that due to the first one may be depressed by fluorination. Electronic polarizability can be estimated by measuring the refractive index of the liquid at frequencies of visible light.[5] Highly fluorinated compounds are known to have smaller refractive indices than those of their parent compounds.

When the boiling points of halogenated acetic acids are correlated with refractive indices (n), a good linear-like correlation is observed as shown in Fig. 2. Similar to the case of acetic acids, 27 series of organic compounds also showed linear correlations of the boiling points vs n;[2] selected slopes, intercepts, and correlation coefficients (r) are summarized in Table 1. So long as the structures of a series of molecules resemble each other, these linear correlations have fair to excellent correlation coefficients.[4,6]

The present linear relation between refractive index and boiling point would be justified as follows. Based on the theoretical relation between interaction energy of molecules and n,[4] the boiling point (bp) would be expressed as a function of n, as follows:

$$\mathrm{bp} = \mathrm{f}(n) = A((n^2-1)/(n^2+2))^2 + B(n^2-1)/(n^2+2) + C$$

Here, A is the constant concerning London interaction, B is that for Debye interaction, and C is the interaction energy independent from electronic polarizability. Though the relation of bp with n couldn't be linear in a wide range of n, within the range of $1.3 < n < 1.7$ a good to excellent linear correlation between $(n^2-1)/(n^2+2)$ and n ($r > 0.998$), as well as $((n^2-1)/$

Table 1. List of Correlations of Boiling Points vs Refractive Indices of Substituteded Organic Compounds

Series of compounds	Number of points	Range of n	Slope [K]	Intercept [K]	*r*
1-substituted hexanes	5	1.376–1.492	7.8×10^2	-7.0×10^2	0.983
2-substituted ethanols	8	1.289–1.571	3.9×10^2	-1.6×10^2	0.946
1-substituted acetones	7	1.300–1.470	6.9×10^2	-6.0×10^2	0.988
ethyl substituted acetates	6	1.307–1.503	6.7×10^2	-5.5×10^2	0.902
substituted acetonitriles	7	1.333–1.574	4.4×10^2	-2.3×10^2	0.840
monosubstituted benzenes	5	1.468–1.620	6.7×10^2	-6.2×10^2	0.987
1,2-disubstituted benzenes	13	1.443–1.661	7.2×10^2	-6.6×10^2	0.987
1,2,4-trisubstituted benzenes	30	1.423–1.647	7.8×10^2	-7.4×10^2	0.882

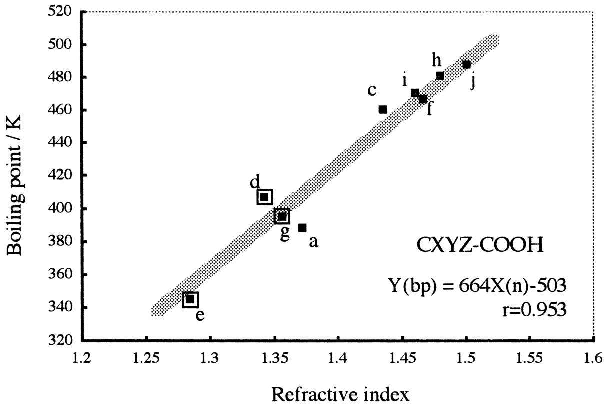

Fig. 2. Boiling points of halogenated acetic acids as a function of refractive index. Double squares are fluorinated acetic acids. a) acetic acid, c) chloro-acetic acid, d) difluoroacetic acid, e) trifluoroacetic acid, f) dichloroacetic acid, g) chloro-difluoroacetic acid, h) bromoacetic acid, i) trichloroacetic acid, j) bromochloroacetic acid.

$(n^2+2))^2$ and n ($r > 0.996$) could be seen. Thus the relation of bp to n is approximately linear in this range, which contains the boiling points of usual organic compounds.

Since the Hildebrand's pioneering work,[9] the correlation of boiling point to refractive index has been widely studied.[7,8,10] Although they had succeeded in prediction of values for several varieties of organic compounds, they had introduced many factors into the relations to get wide applicability and predictability, thus made the relations too complicated for convenient use.[11]

Anyway, the common understanding that "boiling points of organic compounds are mainly depending on their molecular weights" is not satisfactory.[12] The fact that a molecule having a large molecular weight usually has a large molecular orbital and many more electrons suggests a large electronic polarizability, which causes large intermolecular forces and thus results in a high boiling point. Meanwhile, fluorine atoms in the molecule attract orbitals and electrons near by the atomic nuclei,[13] thus they induce a smaller electronic polarizability of the molecule to bring the boiling point lower.

Here we should note that the introduction of fluorine atoms into a molecule is the sole methodology to reduce electronic polarizability that causes isotropic molecular interactions due to electronic polarization. Thus, introduction of a fluorine atom into a molecule should be paid much attention as a method to control anisotropic interactions.[14]

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