Family Plots for Evaluating Physical Properties of Organosilicon Compounds

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Since the early 1960s, serious efforts have been made to improve the reliability of physical property data (Rossini et al., 1967).The propagation of errors, poor data or data of unknown quality leads to wasted resources, over-designed (and needlessly costly) processing equipment, misdirected effort and poor quality products. Evaluation of data by experts can improve data quality tremendously, and data compilations that have been evaluated for reliability and accuracy are becoming more common (Daubert et al., 1991). Evaluation, however, is often a complex and sometimes subjective process. Thus, new approaches to evaluation can be valuable for supplementing existing methods. The procedure outlined here, although useful primarily for evaluating data for accuracy and consistency, can sometimes be used also for predicting properties of family members.

For organosilicon compounds (and organometallic compounds in general), physical property data are often incomplete and of variable quality. Literature values for the boiling point of such a well-known substance as hexamethyldisiloxane, for example, range from 92 to 110°C. Reported heats of formation vary from -775 to $-1{,}080$ kJ/mol (-185 to -258 kcal/mol). Properties reported for less common materials often show even larger discrepancies.

Prediction of properties that have not been or cannot be measured may be important for engineering design or other purposes. Many useful schemes have been developed for predicting physical and thermodynamic properties of organic compounds (Reid et al., 1987; Danner and Daubert, 1989). Predictive methods based on the principle of corresponding states, or on group contribution or bond additivity concepts are capable of producing excellent results, but need reliable experimental data from which the predictive parameters are derived. If good data are not available, compiling reliable constants for the atomic, bond and group contribution methods such as was done by Myers (1990) becomes difficult and the reliability of the predictions suffers.

Discussion

For homologous series of organic compounds, many properties form a smooth curve when plotted against molecular weight. Common examples are the boiling points of hydrocarbons and densities of oligomers. We designate such plots as "series" plots, where members of the series differ by one substituent group (for example, one CH_2 unit in the group C_nH_{2n+2}).

Family plots, as discussed in this article, refer to related compounds in which three substituent groups X, Y and Z are varied (for example, Ph, Me and Cl on Si) and the property values are plotted as a function of molecular weight. The result is a triangular plot with SiX_4, SiY_4, and SiZ_4 at the apexes. Family plots would seem to be obvious extension of series plots, but apparently have not been previously reported. Family plots provide a convenient method of evaluating existing data and for predicting properties of compounds within the family, provided those properties are known reliably for at least some family members. This method may be less useful for organic compounds, because many members of natural families are not known, or are of little interest.

This procedure is not just a graphical group contribution method; the molecular weight provides an additional constraining parameter. Two advantages over algebraic methods can be cited: the visual display makes it easier to discover discrepancies in the data, and the plots are useful for both additive and nonadditive properties. Placement of the curves may seem arbitrary, but is constrained by several factors. Tie lines, which connect corresponding points on the perimeters, parallel the perimeter lines, and must intersect at the proper molecular weights of the mixed substituent compounds represented by the interior points. These constraints make it possible to pinpoint anomalies in the data, provided at least a few points of known reliability are available. The method is especially useful for predicting the properties of mixed substituent compounds.

Plots are constructed using only carefully evaluated data. Then smooth curves are drawn through the points representing each series of compounds. Often one or more anomalous points immediately become evident (see examples below). Most often such discrepancies can be traced to experimental, calculation, or typographical errors. Some excursions are real, however, and are explainable by some unexpected physical effect.

Properties to which this concept have been successfully ap-

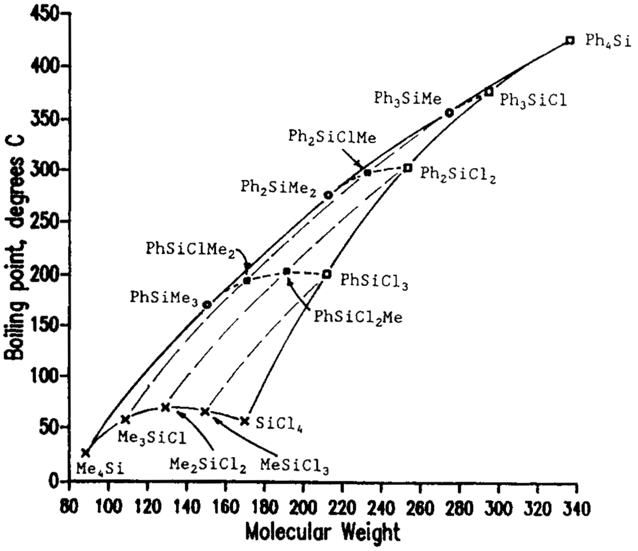

Figure 1. Boiling points of methylphenylchlorosilanes.

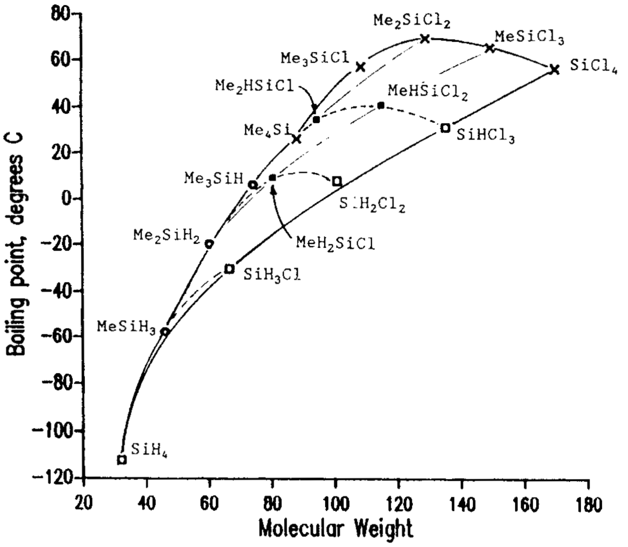

Figure 2. Boiling points of methyl(hydrogen)chlorosilanes.

plied are boiling point, critical properties, heat of formation, free energy of formation, entropy, heat of vaporization, ideal gas heat capacity and liquid density. Some of these properties are additive functions and give linear plots against molecular weight; others form nonlinear but smooth continuous curves.

Property Correlations

Normal boiling points

Evaluation of boiling temperature data is often done by series plots. Prediction methods have been reviewed by Lyman et al. (1982); none are completely satisfactory. A family plot for the methyl phenyl chlorosilane family is shown in Figure 1. Reliable values are known for all compounds in the family and the chart illustrates a typical plot for a nonlinear property.

Another family, the methylchlorosilanes, is shown in Figure 2. This plot bears only slight resemblance to the prototype triangle, but the point for H_2SiCl_2 appears to be high. The reason is not apparent. Vapor pressure data from several independent sources support a boiling point of 8.4±0.1°C, so it is unlikely to be in error. One might conjecture that the boiling point of $HSiCl_3$ is low, but it is well documented from a multitude of reliable sources. One possibility is that H_2SiCl_2 may partially dimerize, which in effect would increase the average molecular weight and the boiling point. Further studies on this material are indicated.

Critical properties

Critical properties are difficult to measure accurately, and results are sensitive to impurities. Also, the compound being observed may decompose before it reaches the critical temperature. Most predictive methods use the normal boiling point plus a set of group contributions whose values depend on the structure of the molecule (Gambill, 1959; Reid et al., 1987; Fisher, 1989). These group contributions, however, include only a few parameters for organosilicon compounds. Some data are available for the Lyderson method (Reid et al., 1977), which usually gives good results for organosilicon monomers and siloxane oligomers up to Si_4 (Flaningam, 1986). Grigoras (1990) has proposed an *a priori* method, based only on molecular surface interactions, to calculate *Tc*, *Pc*, *Vc*, and density. His standard deviation for *Tc* is 16.4°C or 2.9%, and for *Pc* it is 3.1 bar.

A plot for critical temperatures of the PhMeClSi family is shown in Figure 3. Our value (797 K) for $Ph_2MeSiCl$ appears high by about 22°. The value for Ph_2SiCl_2 also appears slightly high.

Among methods for estimation *Pc*, the Lyderson method (Reid et al., 1977) is useful for organosilicon compounds. Estimations of *Pc* are less accurate than those for *Tc*; the Lyderson method gives an observed error of 12% at the 95% confidence level.

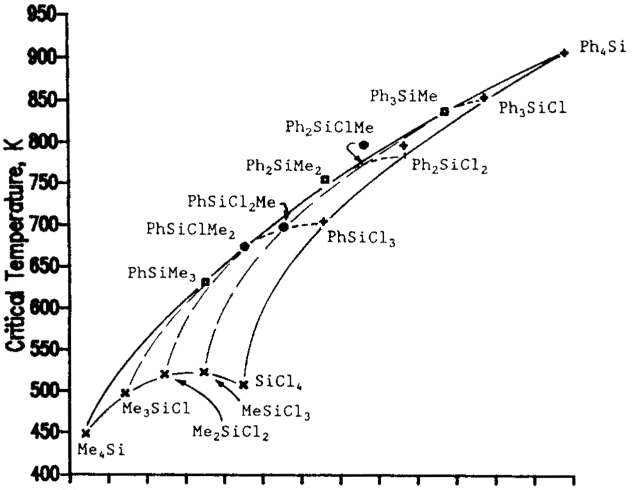

Figure 3. Critical temperatures, methylphenylchlorosilanes.

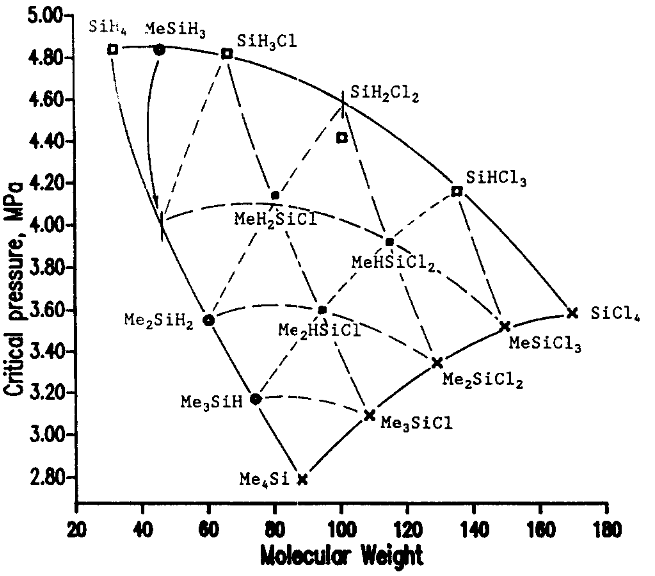

Figure 4. Critical pressures, methyl(hydrogen)chlorosilanes.

Critical pressures for the HMeClSi family are shown in Figure 4. Clearly the point for $MeSiH_3$ is high and is probably in error. This observation is supported by our own independent evaluation of vapor pressure and boiling point data from the literature. (The correct value is 4 MPa). Since critical pressure is difficult to measure more closely than about ±10%, correlation of the other points in Figure 4 is felt to be satisfactory.

Standard heat of formation

This property is defined as the heat used in forming the material in its standard state from the elements in their standard states. This property is particularly difficult to measure accurately for organosilicon compounds, as it is usually based on the heat of combustion. Incomplete combustion, formation of SiC and other undesirable products, as well as uncertainty as to the thermodynamic state of the resulting (hydrated) SiO_2 all contribute to the large spread of values reported in the literature. Special designs for combustion bombs (Good et al., 1964; Hajiev and Agarunov, 1968; Voronkov et al., 1988), often combined with additions of fluorinated compounds to give known combustion products, have reduced the variability of the measurements significantly. Heats of reaction, equilibrium constants (Doncaster and Walsh, 1986; Walsh, 1987) and kinetic measurements (Walsh, 1987) can be used to derive heats of formation when reliable data are available, but such examples are infrequent.

Group and bond methods for predicting this property have been documented by Mosin (1976), Kanovich et al. (1982), Meyers (1990), O'Neal and Ring (1966, 1981), and Luo and Benson (1989). Danner and Daubert (1989) and Meyers (1990) have compared group methods and bond methods. Pedley (1972, 1977) has compiled a self-consistent collection of thermochemical data for organosilicon compounds, based on the least-squares analysis of many thermochemical reactions. Walsh has critically reviewed the data on silicon halides (1983) and methyl silanes (Doncaster and Walsh, 1986), and has given a good review of the field (1989).

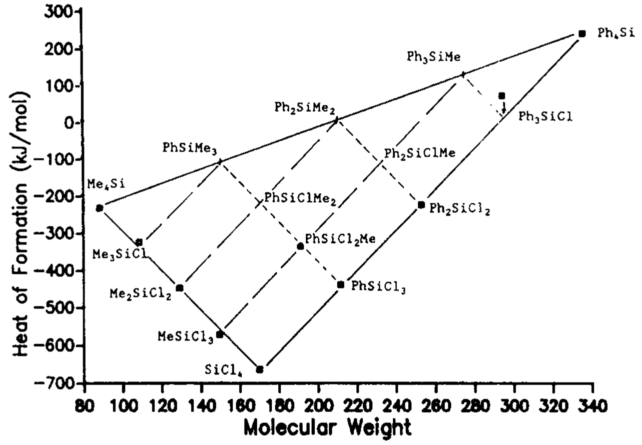

Figure 5. Heats of formation, methylphenylchlorosilanes.

Family plots confirm that group contributions are essentially additive, with second-order interactions small. This finding is consistent with reports by Luo and Benson (1989) and O'Neal and Ring (1981). Small nonlinearities arise from an electrostatic term that can be calculated (O'Neal and Ring, 1981; Benson and Luria, 1975). Group and bond methods do not usually include second-order interactions.

The family plot for ClMePhSi compounds is shown in Figure 5. The value for Ph_3SiCl is high; it should fall at 0. It is easy to predict values for the $Ph_xMe_{4-x}Si$ series, and for the mixed substituent compounds $PhMe_2SiCl$, $PhMeSiCl_2$, and $Ph_2MeSiCl$ from the intersections of the tie lines at the appropriate molecular weight. A similar plot for methylchlorosilanes shows that the accepted value for MeH_2SiCl is high by about 45 kJ/gmol.

Heats of vaporization

The family plot of Figure 6 clearly shows anomalous values

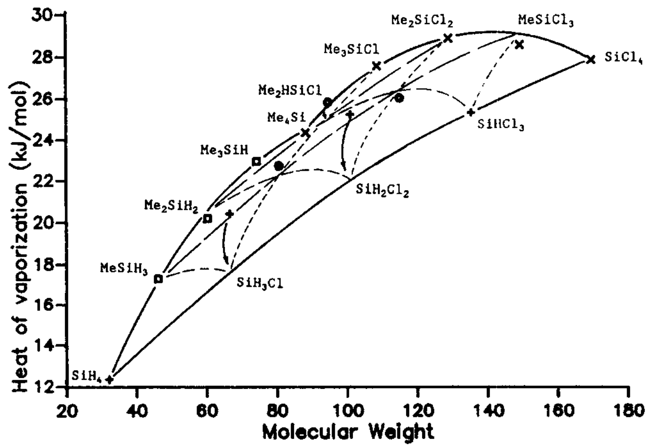

Figure 6. Heats of vaporization of methyl(hydrogen)-chlorosilanes at their normal boiling points.

Table 1. Literature Values of Physical Properties Used to Construct the Figures*

Compound	MW	B.P. °C	Tc K	Pc MPa	$\Delta H^o_f(g)$ (kJ/mol)/E2	$\Delta Hv(bp)$ kJ/mol
$SiCl_4$	169.9	56.9	507	3.593	−6.6275	27.8
$HSiCl_3$	135.5	31.9	479	4.17	−4.9622	25.3
H_2SiCl_2	101.0	8.4	449	4.43	−3.2049	25.2
H_3SiCl	66.6	−30.4a	398b	4.832b	−1.419c	20.4a
H_4Si	32.1	−112.1	269.7	4.8433	+0.343	12.4
Me_4Si	88.2	26.6	450.4	2.814	−2.332	24.3
Me_3SiCl	108.6	57.3	499	3.11	−3.528	27.5
Me_2SiCl_2	129.1	70.2	520	3.36	−4.483	28.8
$MeSiCl_3$	149.5	66.4	517	3.53	−5.718	28.5
Me_3SiH	74.2	6.7	432.0	3.19	−1.5661	22.9
Me_2SiH_2	60.2	−19.6	402.0	3.56	−0.947	20.2
$MeSiH_3$	46.1	−56.9	352.5	4.84	−0.291	17.3
$MeHSiCl_2$	115.1	41.6	490	3.93	−4.02	26.0
Me_2HSiCl	94.6	36	479	3.61	−2.926	25.8
MeH_2SiCl	80.6	8.7	449	4.15	−1.4420	22.7
$PhSiCl_3$	211.6	201.8b	705b	2.84b	−4.396b	
Ph_2SiCl_2	253.2	304b	796b	2.43b	−2.301	
Ph_3SiCl	294.8	378d	854b	1.89b	0.641e	
Ph_4Si	336.5	428f	905b	1.63b	2.311g	
$PhSiMe_3$	150.3	171h	632b	2.46b		
Ph_2SiMe_2	212.4	277i	755b	2.03b		
Ph_3SiMe	274.5	358b	838b	1.84b		
$PhMeSiCl_2$	191.1	204j	698b	2.786b	−3.370b	
$PhMe_2SiCl$	170.7	195k	675b	2.503b		
$Ph_2MeSiCl$	232.8	299b	797b	2.3000b		

*Data for methyl silanes, methyl chlorosilanes and chlorosilanes are from the DIPPR compilation (Daubert and Danner, 1991). References for other data sources are given in parentheses following the property value.
(a) Wintgen (1919).
(b) Dow Corning Corp., Unpublished data (1985–89).
(c) Chase, Jr. et al. (1985).
(d) Rochow and Gilliam (1945).
(e) VanDalen and VanDenBerg (1970).
(f) Florin and Mears (1955).
(g) Klyuchnikov et al. (1977).
(h) Nasielski and Planchon (1960).
(i) Mills and Becker (1956).
(j) Andrianov et al. (1972).
(k) Eaborn (1953).
(l) O'Neal and Ring (1966).

for H_2SiCl_2 and H_3SiCl. The former is no doubt due to the same phenomenon responsible for the anomalous boiling point; the latter may arise simply from inaccurate vapor pressure data—the only literature report (Wintgen) is dated 1919.

Conclusions

Plots of property vs. molecular weight for families of organosilicon compounds show useful regularities. These plots can be used to evaluate the internal consistency of existing data, and often to predict properties for other compounds in the family. The method applies to many thermodynamic and physical properties.

Acknowledgments

Data for methylchlorosilanes were taken from the DIPPR compilation (1991). All data used in the figures are tabulated, along with references to their sources, in Table 1.

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