

PREDICTING LIQUID DENSITIES OF ORGANIC COMPOUNDS
I. HALOGENATED AND OXYGENATED

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Abstract

A new model has been developed and applied for correlating and predicting liquid densities near 20 °C. While extensive tabulations of liquid densities exist, there are many exotic and highly toxic chemicals not included for obvious reasons. The products of liquid density and molecular weight were found to be linear functions of number and types of carbon atoms in the molecule. Increments provided by halogens and oxygens were best described by quadratic functions. Oxygen increments were independent of types of functional groups, including polar and hydrogen bonding molecules.

I. Introduction

In developing a mathematical model that could be used to predict adsorption capacities of carbon beds for organic vapors, liquid densities were needed as input. Although extensive tabulations of liquid densities exist,^{1,2} not all of the hundreds of thousands of possible organic compounds are included. Furthermore, look-up tables are not very efficient for computer calculations.

Methods of calculating liquid densities at various temperatures have been developed.^{2,3} However, these require input of physical data, such as critical temperatures and pressures, and/or a reference experimental density at some temperature. Again, such data are available for only some liquids. The goal of the efforts reported here was to find a way of estimating liquid densities from a minimum of information.

We were interested, at least initially, only in liquid densities near normal ambient temperatures. The CRC Handbook of Chemistry and Physics lists densities for many liquids, usually

at 20 °C.¹ We used values reported within the 19-25 °C range.

II. Empirical Correlations for Hydrocarbons

Figure 1 shows plots of liquid densities versus number of carbon atoms for saturated and unsaturated straight and branched chain hydrocarbons. We found that when liquid density times molecular weight (LDxMW) was plotted against number of carbon atoms, the results converged into a linear correlation (Figure 2). Intuitively, it would be expected that density would be proportional, rather than inversely proportional to molecular weight. However, the latter produced a function independent of 1) number of hydrogen atoms and 2) types of bonds in a hydrocarbon molecule.

When this approach was applied using data for purely cyclic and aromatic hydrocarbons, similar results were obtained (Figures 3 and 4). However, the slope of the LDxMW versus number of carbon atoms plot was higher. This is reasonable, since a cyclic structure is more compact and would result in greater density. The LDxMW values for hydrocarbons containing both straight/branched carbons and cyclic/aromatic carbons were intermediate, as would be expected.

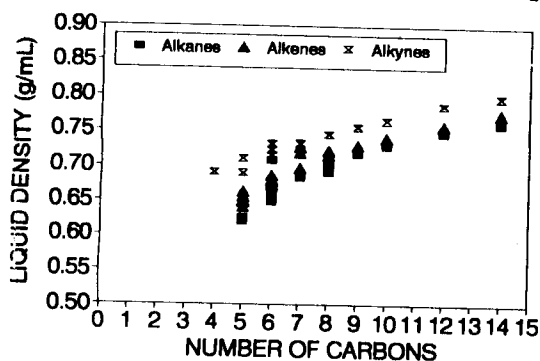


Figure 1.

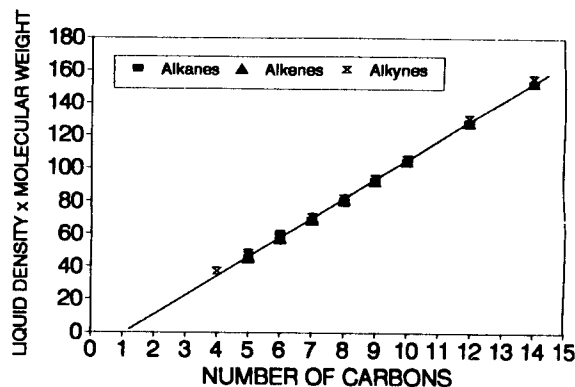


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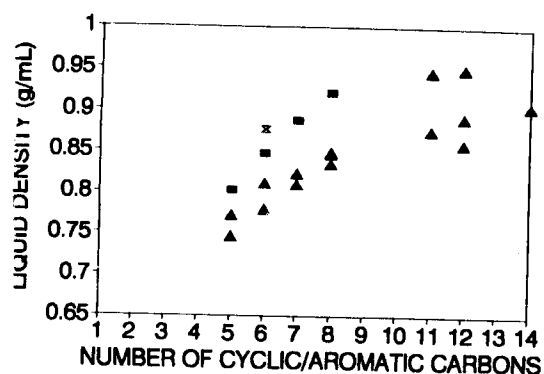


Figure 3.

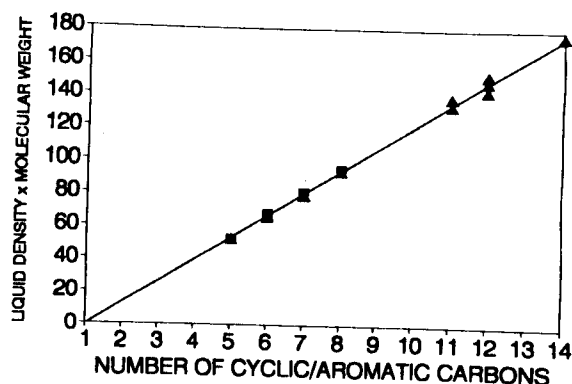


Figure 4.

Using these empirical relationships, densities of 105 hydrocarbons (46 straight/branched, 20 cyclic/aromatic, and 39 mixed) were correlated to give:

$$\text{Liquid Density (g/mL)} = \frac{(11.639*C + 13.803*CC - (12.104*C + 17.128*CC))}{(C + CC)/MW}$$

where C is the number of carbons not part of a ring, CC is the number of cyclic carbons, and MW is molecular weight. The correlation constants were obtained by fitting this equation using a nonlinear curve fitting program (SYSTAT from SYSTAT, Inc., Evanston, IL) on an IBM-PC compatible desktop computer. The standard deviation of 105 experimental points from this correlation was 0.017 g/mL. Calculated and experimental densities are compared in Figure 5.

III. Extension to Halocarbons

The next step was to observe the effect on liquid densities of replacing hydrogen atoms on hydrocarbons with chlorine atoms. Figure 6 shows that chlorines shift the intercept, but do not affect the slope, of the LDxMW vs C plot. This shift is more than linear with the number of chlorine atoms. The same result was observed for chlorinated cyclic and aromatic hydrocarbons.

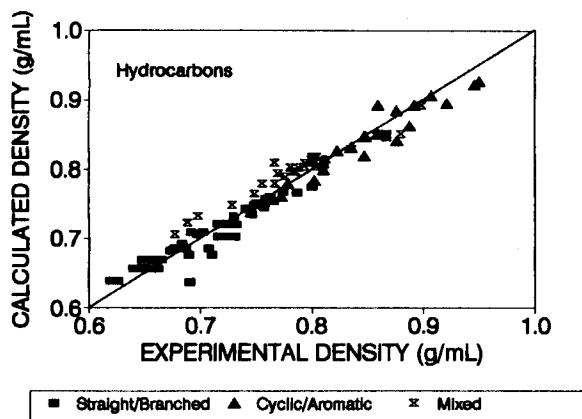


Figure 5.

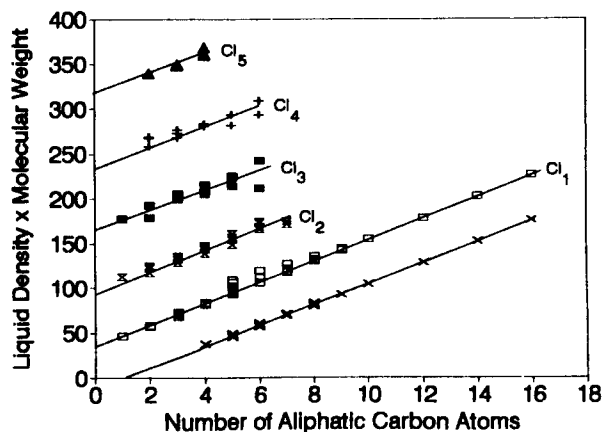


Figure 6.

The correlation equation was extended to include the number of a second heavy atom, X:

$$\text{Liquid Density (g/mL)} = \frac{(11.639*C + 13.803*CC + S*X + Q*X^2 - (12.104*C + 17.128*CC + I*X))}{(C + CC + X)/MW}$$

Correlation coefficients S, Q, and I for fluorocarbons, chlorocarbons, bromocarbons, and iodocarbons are listed in Table 1. Standard deviations of the data fits ranged from 0.043 g/mL for fluorine, the lightest halogen, to 0.113 g/mL for iodine, the heaviest.

TABLE 1.

Liquid Density Coefficients for Hydrocarbons

Class	Number of Data	Coefficients			Standard Deviation (g/mL)
		S	Q	I	
Straight/ Branched (C)	105	11.639	0	12.104	0.017
Cyclic/ Aromatic (CC)		13.803	0	17.128	
Oxygenated	172	21.523	1.486	3.658	0.052
Fluorinated	22	51.522	-0.417	166.160	0.043
Chlorinated	126	52.720	3.036	31.032	0.054
Brominated	56	85.567	34.472	-127.687	0.095
Iodinated	33	131.644	102.962	-170.761	0.113

Figures 7-10 show comparisons of calculated and experimental densities. Note: The correlations do not yet include mixed halocarbons, e.g., chlorofluorocarbons.

IV. Extension to Oxygenated Hydrocarbons

Unlike halogens, oxygen atoms can be incorporated into hydrocarbon structures in a variety of functional groups, forming alcohols, aldehydes, ketones, esters, ethers, acids, and epoxides. These classes of oxygenated compounds exhibit wide differences in polarity and hydrogen bonding, which would be expected to significantly affect liquid density. Figures 11 and 12 show the surprising result that liquid densities of oxygenated hydrocarbons can again be correlated by structure alone, ignoring polarity and hydrogen bonding properties.

The effect of multiple oxygens in straight/branched chain hydrocarbons is shown in Figure 13 to be similar to that seen for chlorine. Intercepts of LDxMW versus C are shifted more than linearly for increasing numbers of oxygen atoms; the slope is essentially unchanged.

Correlation coefficients given in Table 1 were obtained using densities for 172 oxygenated hydrocarbons, representing the classes of compounds listed above. The standard deviation of the fit was 0.052 g/mL. Figure 14 shows a graphical comparison of calculated and experimental values. Note: The correlations do not yet include compounds where oxygen is incorporated into a ring structure.

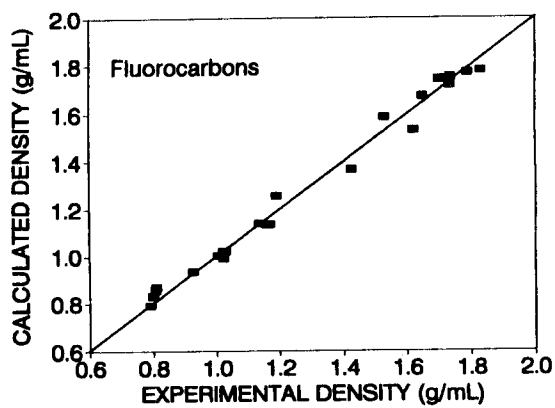


Figure 7.

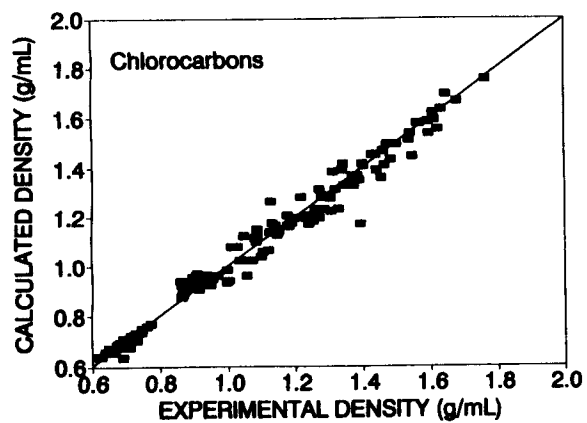


Figure 8.

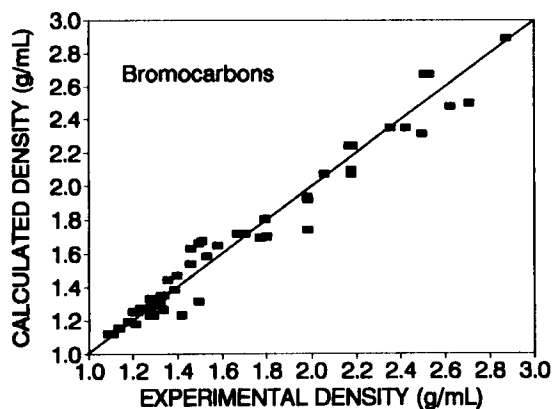


Figure 9.

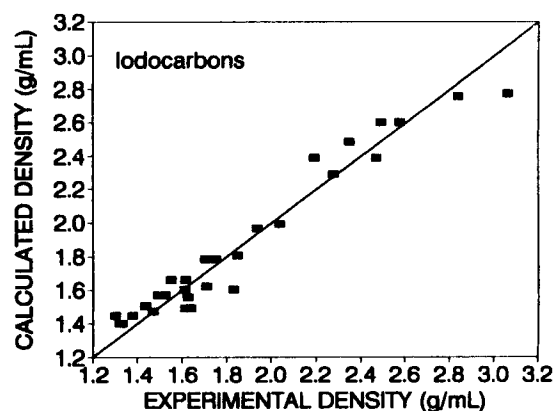


Figure 10.

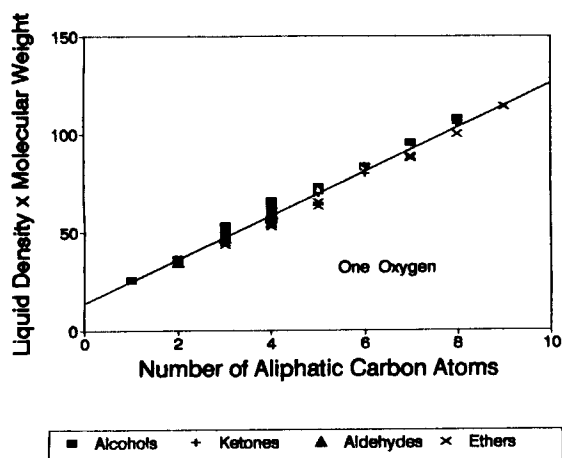


Figure 11.

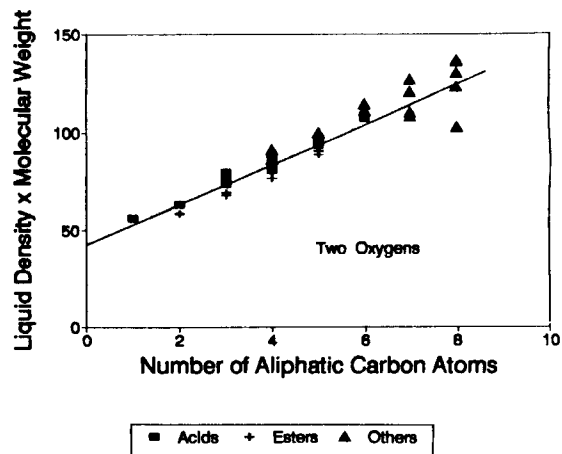


Figure 12.

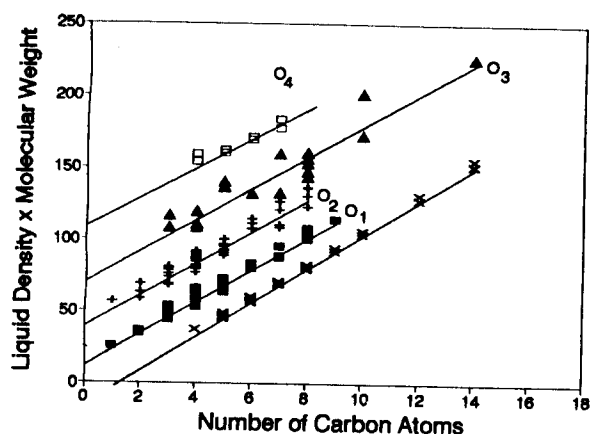


Figure 13.

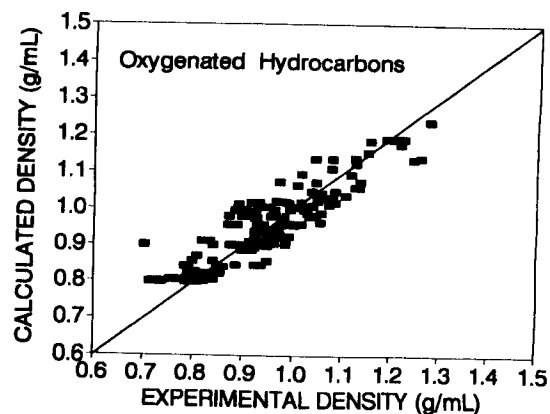


Figure 14.

CONCLUSIONS

Correlations have been developed for estimating densities of liquids near 20 °C. The only information that needs to be known is: 1) carbon atom number and type (cyclic or not) and 2) other heavy atom number and type (F, Cl, Br, I, O). Effects of polarity and hydrogen bonding have not been observed in these correlations, but may provide second-order improvements in these estimates. Applications of these correlations include: 1) Checking reported densities. [Some suspicious values have been found in Reference 1.] 2) Calculating unknown densities, such as for exotic or highly toxic liquids. 3) Calculating by computer other properties, such as carbon adsorption capacity, that require liquid density as input. [This avoids the inefficient use of look-up tables.]

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1. Weast, R. C., ed., CRC Handbook of Chemistry and Physics, 67th Edition, pp C42-C553, CRC Press, Inc., Boca Raton, Florida (1987).
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